GEOCHEMICAL PROCESSES IN THE GASCOYNE LIGNITE MINING AREA, BOWMAN COUNTY, NORTH DAKOTA

By Donald W. Fisher, Donald C. Thorstenson, Mack G. Croft, and Robert L. Houghton

CONTENTS

ILLUSTRATIONS

CONVERSION FACTORS

Coal mine production data are reported in short tons. To convert these data to SI units:

Multiply	by	to obtain
short tons	907.18474	kilograms (kg)

(The relationship is exact - the multiplier serves to define the mass of a short ton.)

Gas pressures are reported in atmospheres, a unit which is useful in chemical thermodynamics and is easily related to compositions of the lower troposphere. To convert to other systems,

Multiply	by	to obtain
atmospheres (atm)	101,325	pascals (pa) - SI unit.
atmospheres (atm)	14.70	pounds per square inch (psi) - Inch-pound unit.

Other units used in the report can be converted to inch-pound equivalents as follows:

Multiply	by	to obtain
millimeters (mm)	0.03937	inches (in)
meters (m)	3.281	feet (ft)
kilometers (km)	0.6214	miles (mi)
hectares (ha)	2.471	acres
square kilometers (km^2)	0.3861	square miles (mi^2)
liters (L)	1.057	quarts (qt)
cubic meters (m^3)	35.31	cubic feet (ft^3)
cubic meters per second (m^3/s)	35.31	cubic feet per second (ft^3/s)
grams (g)	0.002205	pounds, avoirdupois (lb)

National Geodetic Vertical Datum of 1929 (NGVD of 1929):

A geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called "Mean Sea Level."

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ABSTRACT

A study was made of the geochemistry of shallow ground water and the unsaturated zone in the vicinity of the Gascoyne, North Dakota lignite mine. The strip mine currently (1984) produces about 3 million tons per year from the Harmon lignite bed, an extensive, economically important unit in the Tongue River Member of the Paleocene Fort Union Formation.

Test wells were drilled near and in the mine area for water-level measurements and collection of water samples. Ground and surface waters were analyzed for major, minor, and trace constituents; tritium and carbon-13 isotopes; and dissolved gases. Gas samples from several different levels in the unsaturated zone were obtained from six sites, two of which are in reclaimed mine spoils. The gas samples were analyzed for composition, carbon-13, and carbon-14. Mineralogic and cation-exchange data were obtained from core samples, highwell samples, and miscellaneous surface solids. Chemical compositions of three Harmon lignite samples were determined.

Reactions that control ground-water chemistry in the Gascoyne area include oxidation of organic matter and ferrous iron minerals in the unsaturated zone and in the upper water table; dissolution of carbon dioxide, carbonate minerals, gypsum, and sodium-magnesium sulfates in unsaturated-zone water; cation-exchange reactions on clays and on lignite; sulfate reduction and pyrite deposition in lignite below the water table; leaching of halides and organic matter from the lignite; and dissolution of silicates, which produces highly alkaline ground waters near the lignite outcrop.

Carbonate-mineral dissolution apparently is sufficient to maintain ground-water pH values near or above 7 throughout the mine area. Development of strong mineral acidity in the waters by pyrite oxidation is unlikely in the present hydrogeologic environment. Continued mining of the lignite will increase the total amount of sodium sulfate in ground-water discharge to the North Fork Grand River drainage system.

INTRODUCTION

The study area (site 10 in fig. 1) includes about 100 square kilometers (roughly 40 square miles) of Bowman County, in the unglaciated part of the Northern Great Plains in southwestern North Dakota. Lignite mining and agriculture are the chief economic activities in the Gascoyne area. Leonardite[1] from the Gascoyne mine is processed in an American Colloid Company plant about 1.5 km south of the mine.

The Gascoyne mine is one of a number of active strip mines in the Northern Great Plains coal regions at which production was greatly expanded during the mid-1970's. Mine output at Gascoyne increased more than 10-fold between 1974 and 1977.

Acknowledgments

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[1] Leonardite is a waxlike, black or brown, colloidal vitreous material formed by the oxidation of lignite, particularly the previtrain layers. The material can be extracted from weathered lignite with alkaline solutions, and has been used in making wood stains and dye. It has the property of swelling and forming a gel and is used as a stabilizing agent in well-drilling fluid.
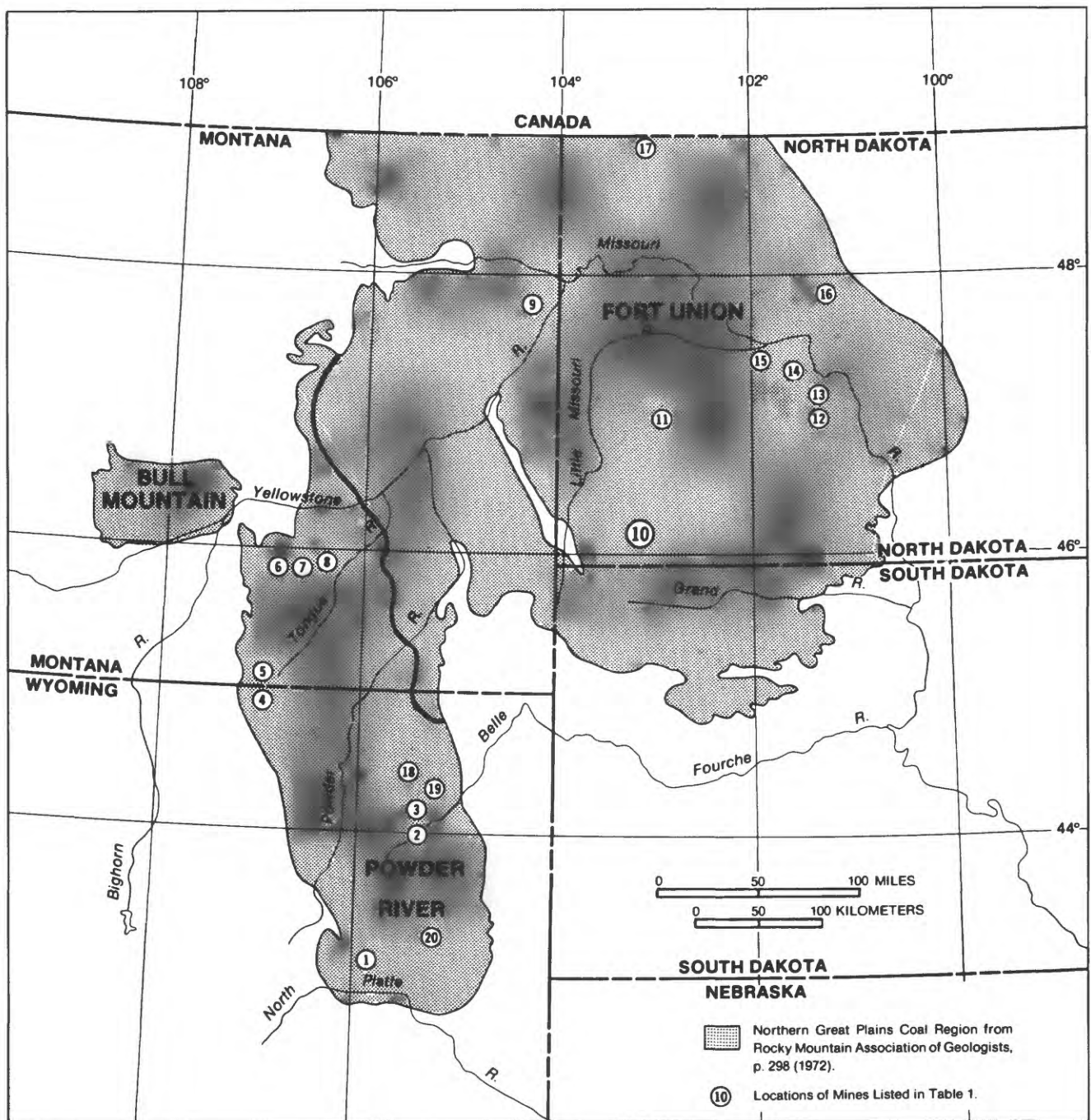
Figure 1. Location of Northern Great Plains coal region and mine areas
(modified from Rocky Mountain Association of Geologists, 1972)

Purpose and Scope

A preliminary reconnaissance study suggested that current strip mining activities at Gascoyne could affect the quality of surface water and ground water in the area (Ground-Water Subgroup of Northern Great Plains Resources Water Work Group, 1974).

The purpose of this report is to present the results of a study to identify, measure, and evaluate changes in water quality that may have already occurred as a result of strip mining at Gascoyne, and the potential for further changes as mining continues.

Test wells were drilled near and in the mine area for water-level measurements and collection of water samples. Water samples were analyzed for ionic constituents, tritium and carbon-13 isotopes, and dissolved gases. Gas samples were obtained from various depths in the unsaturated zone at six sites. The gas samples were analyzed for gas composition, carbon-13, and carbon-14. Mineralogic and cation-exchange data were obtained from core samples, highwall samples, and miscellaneous surface solids. Chemical compositions of three samples of the Harmon lignite were determined

Well-Numbering System

The wells and test holes referred to in this report are numbered according to a system of land survey in use by the U.S. Bureau of Land Management and the U.S. Geological Survey. The U.S. Bureau of Land Management system is illustrated in figure 2. The first numeral denotes the township north of a base line, the second numeral denotes the range west of the fifth principal meridian, and the third numeral denotes the section in which the well is located. The letters A, B, C, and D designate, respectively, the northeast, northwest, southwest, and southeast quarter section, quarter-quarter section, and quarter-quarter-quarter section (10-acre or 4-ha tract). For example, well 131-099-15DAA is in the NE 1/4 NE 1/4 SE 1/4 of sec. 15, T. 131 N., R. 099 W. Consecutive terminal numerals are added if more than one well or test hole is recorded within a 10-acre (4-ha) tract.

Climate

The climate of the Gascoyne area is cool and semiarid. The mean temperature at Hettinger, North Dakota, 24 km southeast of the mine, during a 20-year period, 1960-1980, was 5.8°C (Celsius) (fig. 3). Temperatures average 21°C in July and August. Winters are cold; temperatures frequently drop below -30°C. The average growing season is about 125 days.

The mean annual precipitation calculated for Hettinger (fig. 3B) during 1960-1980 was 407 millimeters (mm). About 70 percent of the precipitation falls during the growing season (fig. 3C). Thunderstorms are common in June, July, and August.

131-99-33daa

Sec 33

R.99W.

T.131N.

100 99 98 97

132 131 130 129

N
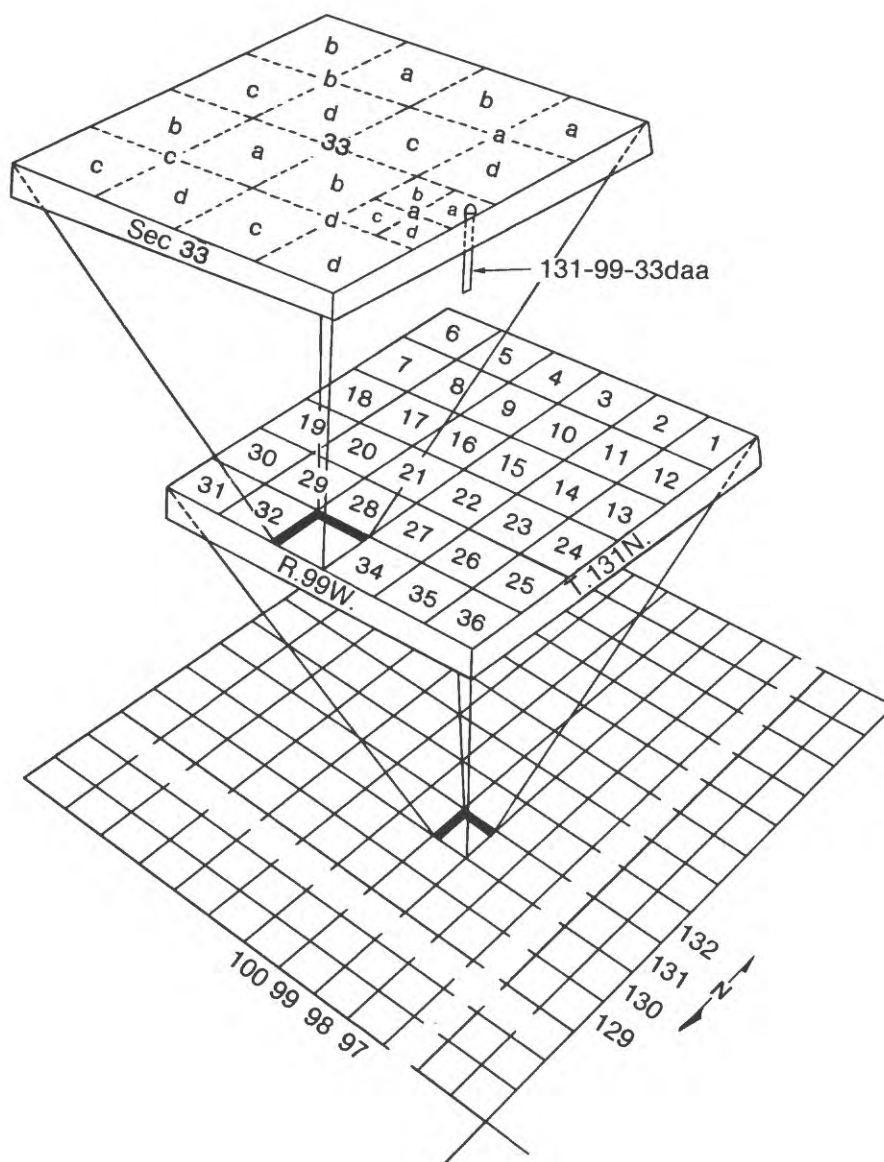
Figure 2. Well-numbering system
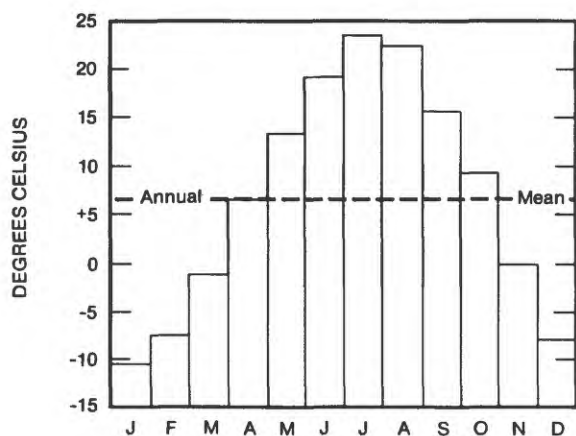
A. — Average monthly temperature
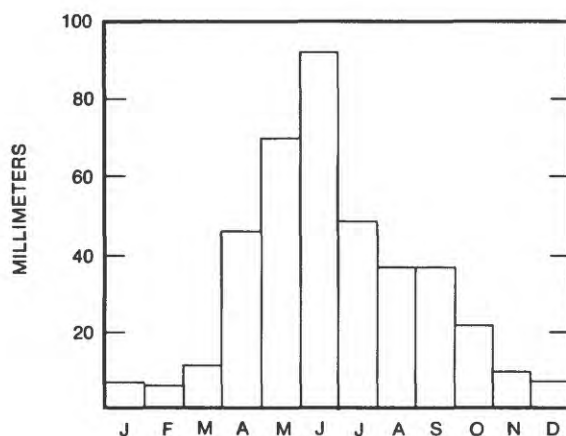
C. — Average monthly precipitation
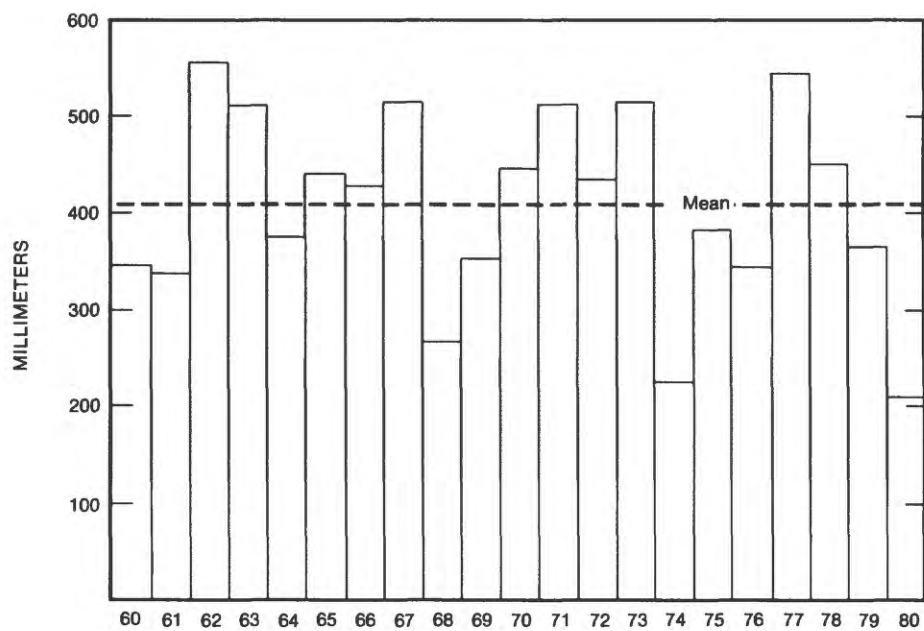
B. — Annual precipitation, 1960-1980

Data from Climatological Data Series, National Oceanic and Atmospheric Administration

Figure 3. Temperature and precipitation at Hettinger, North Dakota, 1960-1980

The years 1974, 1975, and 1976 were exceedingly dry. Extreme drought conditions developed during the summer of 1976 and lasted until the fall of 1977 when unusually heavy amounts of rain fell in late August and September.

Physiography and Drainage

The Gascoyne study area lies within the unglaciated area of the Great Plains. The rolling grasslands have a maximum relief of about 75 m. Highest elevation in the area is about 900 m several kilometers north of the mine. Isolated ridges and buttes are capped by "scoria"--the local term for the residue of baked rock remaining after underground combustion of a lignite seam. The principal stream, Buffalo Creek, drains southeastward into the North Fork Grand River. Drainage is to the Gulf of Mexico by way of the Missouri River.

Many streams in Bowman County have developed a dendritic drainage pattern with larger trunk streams of the system, such as Buffalo Creek, flowing much of their length in northwest-southeast valleys. Tributaries of Buffalo Creek trend north-south and northeast-southwest.

Previous Investigations

Numerous geologic and hydrologic studies, spurred by the search for oil, gas, lignite, and uranium, have been made in southwestern North Dakota and surrounding areas. The earliest geologic investigations pertinent to the report area were made by Lloyd and Hares (1915) and Stanton (1920). Recent geologic investigations have been made by Denson and Gill (1965), Jacob (1975, 1976), and Carlson (1978). Lewis (1977, 1979) made structure contour and isopach maps of the Harmon and Hansen lignite beds in Adams, Slope, and Bowman Counties. The location, mined tonnage, and characteristics of lignite and overburden in Adams and Bowman Counties were described by Kepferle and Culbertson (1955). A soils map of Bowman County was prepared by Opdahl and others (1975). Croft (1974, 1978) described ground-water conditions in Adams and Bowman Counties.

Other reports and environmental studies of interest include a report on spoil banks reclamation by Sandoval and others (1973) and a report on the hydrology and geochemistry at a coal mine at Colstrip, Mont., by Van Voast, Hedges, and McDermott (1977).

Extent of Surface Coal Mining in the Northern Great Plains

According to the U. S. Environmental Protection Agency (1976, p. 4), in excess of 1.5 trillion tons of coal are estimated to underlie the states of Montana, Arizona, Wyoming, Colorado, Utah, North and South Dakota, and New Mexico. About one-half the 160 billion tons of coal considered recoverable in this province is within the Northern Great Plains and is minable by strip-mining methods. Locations of the principal mines in the Northern Great Plains are shown in figure 1. Coal production from these mines more than doubled in 3 years, from 31 million tons in 1974 to 63 million tons in 1977 (Table 1).

Table 1.--Estimated coal production, 1974 and 1977, from mines in the Northern Great Plains[1]

		1974 production (millions of tons)	1977 production (millions of tons)
[2] 1.	Dave Johnston Mine, Wyo.	2.9	3.2
2.	Belle Ayr South Mine, Wyo.	3.3	13.3
3.	Wyodak Mine, Wyo.	.7	.9
4.	Big Horn Mine, Wyo.	.9	2.4
5.	Decker No. 1 Mine, Mont.	7	10.8
6.	Sarpy Creek (Absaloka) Mine, Mont.	1.5	4.5
7.	Big Sky Mine, Mont.	2.7	3.0
8.	Rosebud Mine, Mont.	4.3	9.8
9.	Savage Mine, Mont.	.3	.3
10.	Peerless (Gascoyne) Mine, N. Dak. (study area)	.2	2.7
11.	Lehigh (Husky) Mine, N. Dak.	.2	.1
12.	Center, N. Dak.	1.5	2.1
13.	Glenharold, N. Dak.	1.3	3.8
14.	Beulah (North and South) Mine, N. Dak.	1.7	1.5
15.	Indian Head, N. Dak.	1.2	1.0
16.	Velva Mine, N. Dak.	.5	.3
17.	Noonan Mine, N. Dak.	.5	.5
18.	Rawhide, Wyo. (new 1976)	--	1.1
19.	Cordero, Wyo. (new 1976)	--	2.1
20.	Black Thunder, Wyo. (new 1976)	--	.04
	TOTAL	30.7	63.4

[1] Data sources: Annual Reports of the State Inspector of Mines of Wyoming, reports of the Montana Department of Labor and Industry, the Keystone Coal Industry Manual (published by Informational Mining Services), and personal communications from mining company officials.

[2] Numbers correspond with mine locations shown in figure 1.

History of Surface Mining at Gascoyne, North Dakota

Commercial mining of lignite began in Bowman County, N. D. near Scranton and Gascoyne after the railroad was built in 1907. According to Kepferle and Culbertson (1955, p. 144) the peak year for production of lignite in Bowman County prior to World War II was 1927 when 60,346 tons were produced from four mines, one of which was the Gascoyne mine. The depression of the 1930's nearly ended the mining prosperity of the area; by 1945 production in Bowman County was at a low of 5,121 tons. In 1950 the Knife River Coal Company took over the Gascoyne mine (fig. 4), renamed it the Peerless, and began shipping the lignite to thermal power plants in South Dakota and Minnesota. Between 1950 and January 1975 the Gascoyne (Peerless) mine produced about 100,000 tons per year by strip-mining methods. Most of the mining was in sections 27, 34, and 35, T. 131 N., R. 99 W (see fig. 4). In addition, several small pits had been mined before 1950 in the northeast corner of section 33. The mine was enlarged with opening of pits in sections 28 and 29 in 1975, and production is now about 3,000,000 tons of lignite per year, most of which is burned in the Big Stone generating plant near Sioux Falls, S. Dak. According to the coal company's 30-year mine plan, all lignite in sections 26, 27, 28, 29, 33, 34, and 35, T. 131 N., R. 99 W. will be mined. The mine is presently the second largest in the State of North Dakota, and the operator, Knife River Coal Company, claims it is the most efficient strip mine in the United States with respect to the ratio of strippable coal to overburden.

GEOLOGIC SETTING

Sedimentary rocks in the Gascoyne area were deposited on the south flank of the Williston basin and dip toward the northeast. The near-surface Harmon coal dips gently at about 4 to 6 m/km in this area. The sedimentary deposits have an aggregate thickness of about 3700 m (12000 ft). Only the rocks overlying the Pierre Shale are considered of importance for ground-water supplies in the study area; these formations are discussed in detail by Carlson (1978) and Croft (1978) and consist of alternating beds of semiconsolidated claystone, siltstone, sandstone and lignite. The formations above the Pierre shale, in ascending order, are the Fox Hills Sandstone and the Hell Creek and Fort Union Formations. They range in age from late Cretaceous to early Tertiary. The Fort Union Formation of Tertiary age is the only geologic unit exposed in the Gascoyne area. A brief discussion of the Fox Hills and Hell Creek Formations, and a more detailed description of the Fort Union Formation, are given in the following sections. Clayton and others (1977) have revised part of the Fort Union terminology for use by State personnel in North Dakota, but their revision is not used in this report.

Fox Hills Sandstone and Hell Creek Formation

The Fox Hills Sandstone of Late Cretaceous age consists of interbedded marine grayish-white glauconitic fine- to medium-grained sandstone and greenish-gray claystone. The formation generally is 60 to 90 m thick.
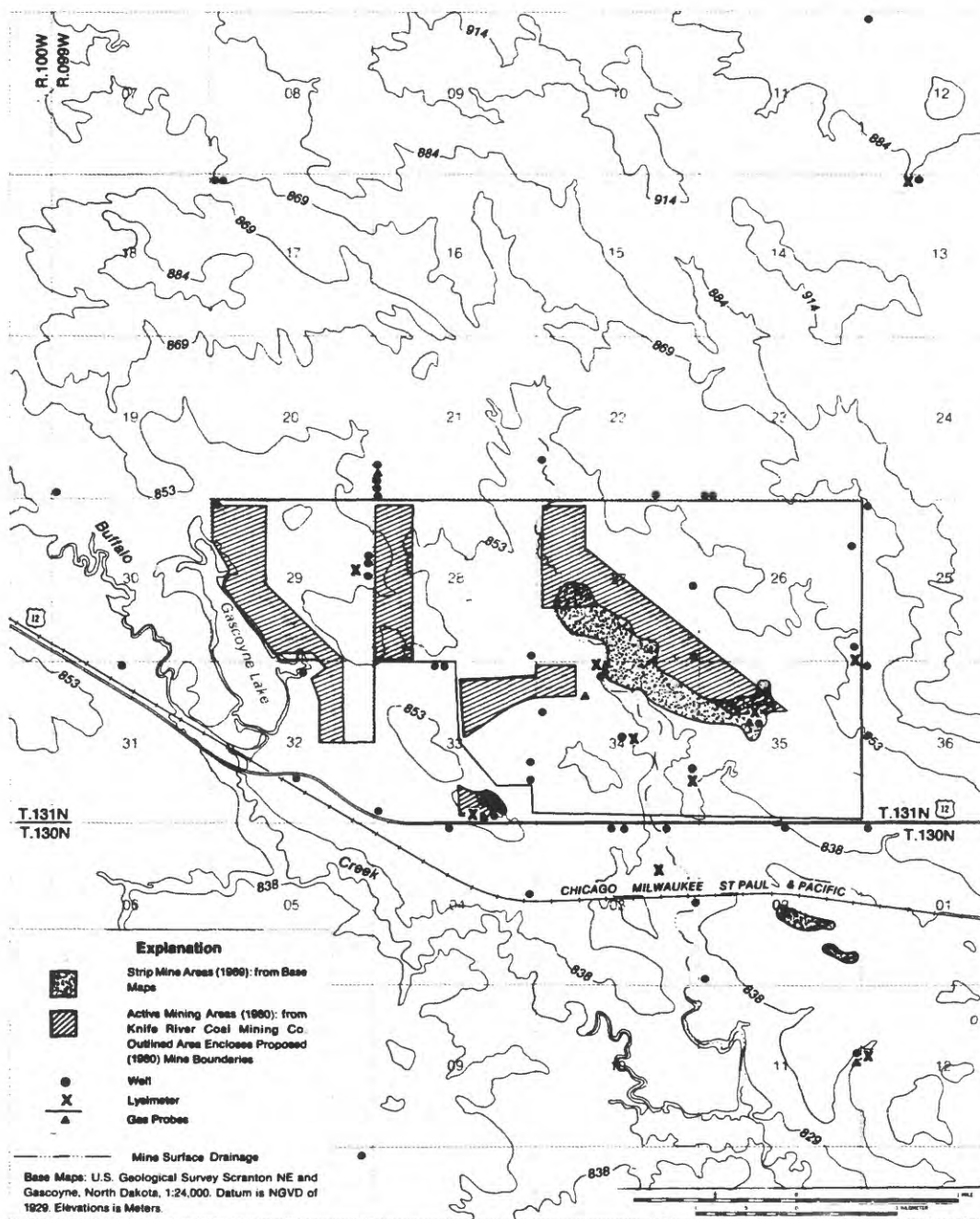
Figure 4. Gascoyne lignite mining area, North Dakota, showing locations of mined areas and sampling points.
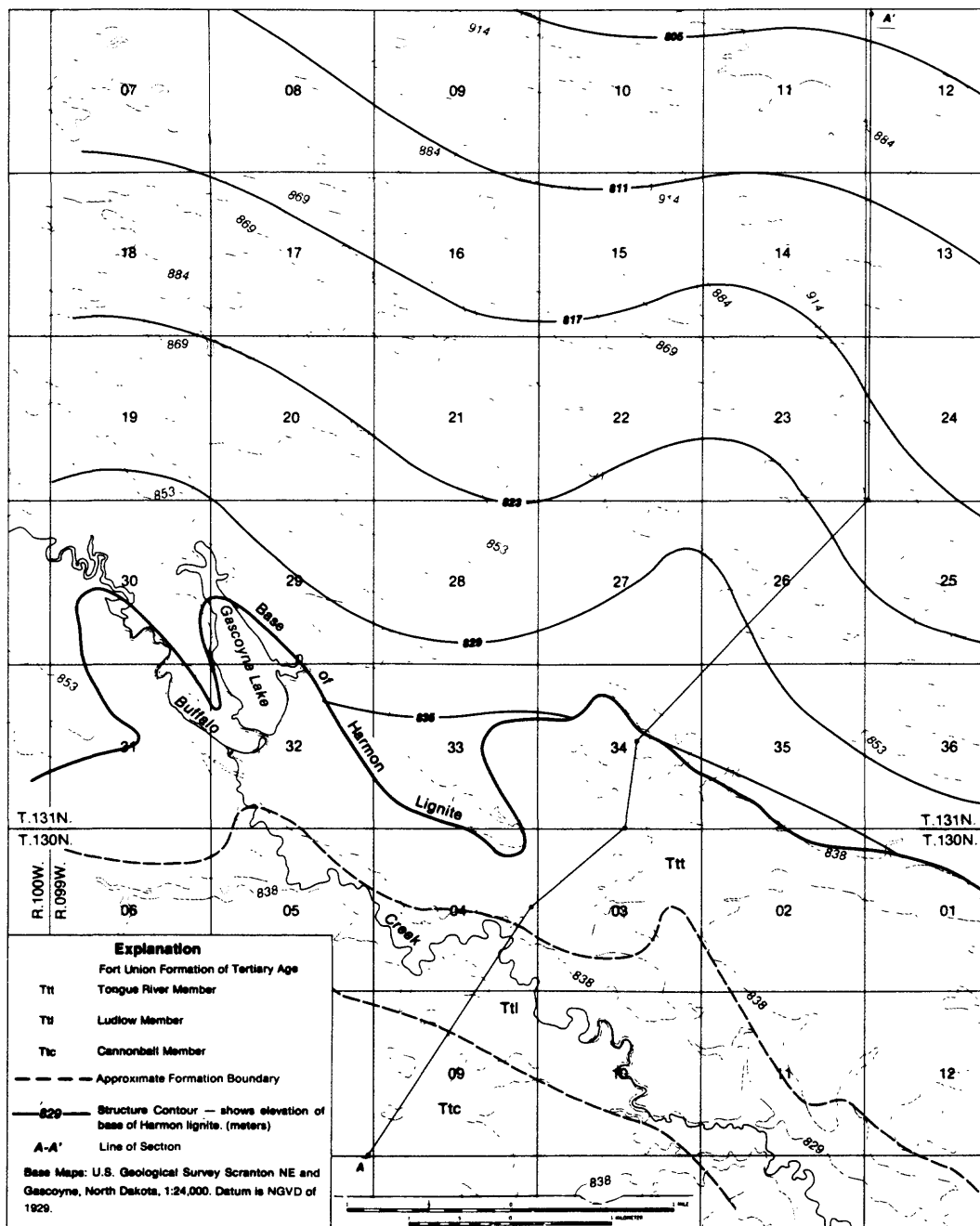
Figure 5. Geologic map of the Gascoyne area, North Dakota, with structure contours on base of the Harmon lignite

-11-

The Hell Creek Formation of Late Cretaceous age consists of continental dark-gray and brown lenticular sandstone and claystone. The Hell Creek is generally 150 to 180 m thick. The formation is divided into three units. The upper unit is predominantly sandstone and siltstone and, together with sandstone in the lower part of the Ludlow Member of the Fort Union Formation, forms the upper Hell Creek-lower Ludlow aquifer. The middle unit is characteristically siltstone and claystone and is a confining bed.

The lower unit is similar to the upper unit and, together with sandstone in the upper part of the underlying Fox Hills Sandstone, is collectively referred to as the Fox Hills-basal Hell Creek aquifer or as the Fox Hills aquifer. Water in this aquifer flows generally from SW to NE. Heads in the Fox Hills aquifer are 15 to 30 m lower than heads in the shallow ground-water aquifers at Gascoyne; the Fox Hills aquifer is present at depths of 370 to 460 m in the study area. Hydrologic and geochemical characteristics of the Fox Hills aquifer are discussed by Croft (1974, 1978); and Thorstenson and others (1979).

Fort Union Formation

The Fort Union Formation of Paleocene age underlies the Gascoyne area and consists of interbedded claystone, siltstone, sandstone, and lignite. In the study area the formation is about 210 m thick and has been divided into the Ludlow, Cannonball, and Tongue River Members (fig. 6). The Ludlow and Tongue River Members are continental deposits; the Cannonball is a marine deposit.

Ludlow Member

Continental rocks of the Ludlow Member, which consist of carbonaceous brown claystone, olive-gray siltstone, yellowish-gray fine-grained channel sandstone, and lignite, crop out as a wide band in the valley of Buffalo Creek (fig. 5). In the Gascoyne area the Ludlow Member (fig. 6) is divided into lower, middle, and upper units by interbedding with the Cannonball Member. The middle unit is about 75 m thick and the upper unit is about 15 m thick.

Cannonball Member

Rocks of the Cannonball Member are the youngest marine strata known in the Northern Great Plains. Deposits crop out in the southwestern corner of the Gascoyne area (fig. 5). The member consists of two beds (fig. 6) of light-olive gray to dark-greenish-gray nearly impermeable claystone and siltstone that interfinger with deposits of the Ludlow. At sec. 17AAA, T.130N., R99W., the lower bed is about 10 m thick. The upper bed is about 18 m thick in well 130-099-4ADD. Drill cuttings from this well contained microplankton which corroborate the marine origin of the deposits (Norman Frederiksen, U.S. Geological Survey, written commun., 1977). Brown (1962) reported that the two beds are exposed in the Little Missouri River Valley north of the study area. The fine-grained deposits of the Cannonball act as confining units.

Figure 6. Geologic section A-A', Gascoyne lignite mine
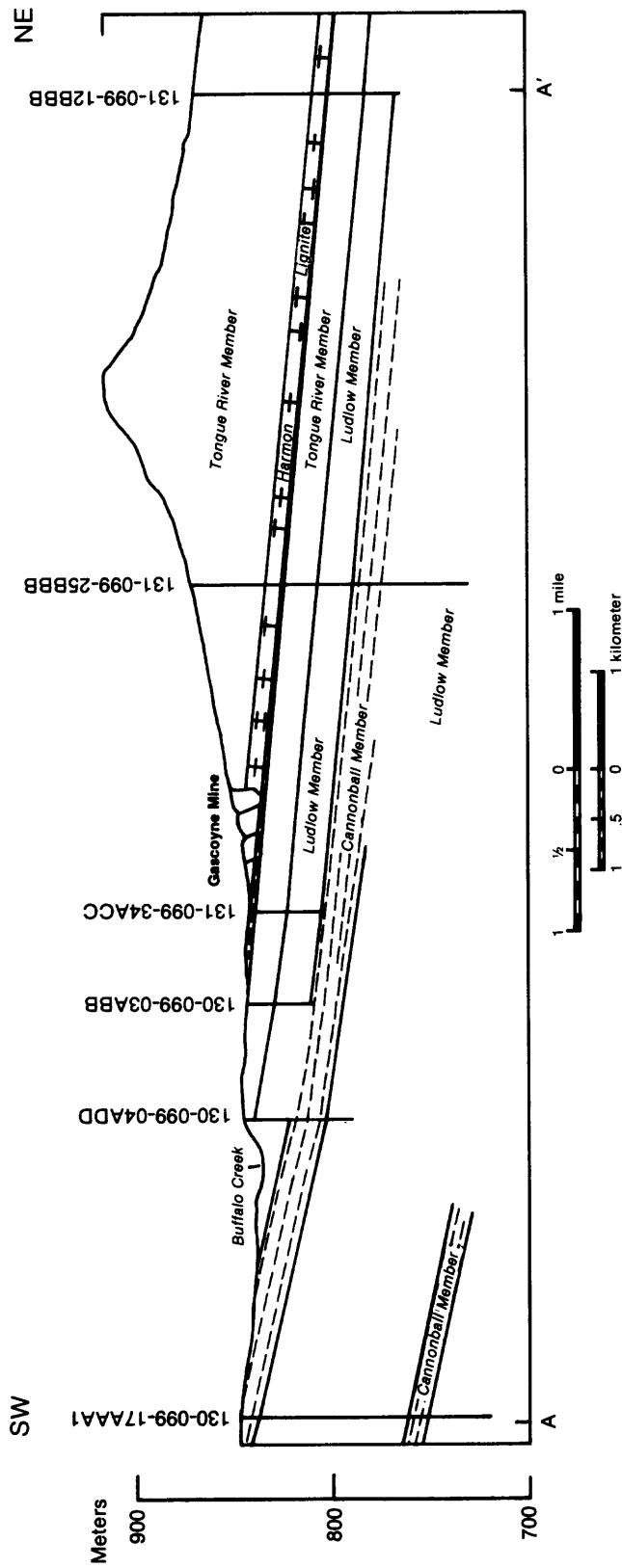
Line of Section from Figure 5.
Control: Test Well Data.

The Tongue River Member consists of continental deposits of Paleocene age that underlie the northern and central parts of the Gascoyne area (fig. 5). The member is about 110 m thick in the study area.

The Tongue River consists of interbedded light-olive-gray to dark-greenish-gray claystone and siltstone, yellowish-gray fine-grained channel sandstone, and lignite. The Harmon lignite, an extensive coal bed about 18 m above the base of the Tongue River in the Gascoyne area, (fig. 6), is about 9 m thick. Rehbein (1978) has recognized the Harmon in the subsurface throughout much of the Williston basin. The Harmon is easily identifiable with gamma-ray logs in test holes. The gamma logs indicate that the lignite is generally less radioactive than overlying and underlying sandstone and claystone. A bed of gray claystone that ranges from 0.3 to 15 m in thickness underlies the lignite (fig. 7). The claystone forms a confining unit beneath the Harmon in the vicinity of the mine. The remaining beds in the lower part of the Tongue River Member consist mainly of permeable fine- to medium-grained semiconsolidated gray channel sandstone. According to Jacob (1976), the sandstone consists largely of quartz, volcanic, and carbonate rock fragments. The deposits above the lignite consist mainly of gray, greenish-gray, and yellow-gray siltstone and claystone. The Hansen lignite, an economically important bed that is mapped elsewhere in the area by Lewis (1977), does not crop out in the vicinity of Gascoyne.

Unconsolidated Deposits of Quaternary Age

Alluvium of Pleistocene(?) and Holocene age overlies the consolidated rocks of the Fort Union Formation beneath Buffalo Creek and its tributaries. The deposits are not shown on the geologic map (fig. 5). Much of the alluvium consists of dark-gray sandy silt and clay eroded from nearby older rocks. The alluvium is probably less than 3 m thick.

Soils of Holocene Age

Prairie Chernozem soils of the Amor-Reeder-Cabba association are developed on the non-alluvial Tertiary deposits in the Gascoyne area to a depth generally less than 1 m (Opdahl and others, 1975). These soils are characterized by a thin grayish-brown loamy A horizon and a moderately permeable neutral or slightly alkaline B horizon. Carbonate deposits are common at a depth of about 1 m. Soils of the Searing and Brandenburg series are developed along the outcrop of the Harmon lignite. They have a characteristically reddish-brown A horizon and a moderately permeable neutral or slightly alkaline calcareous B horizon that extends to a depth of a few meters. The underlying C horizon consists of porcellanite or scoria.

Many of the alluvial deposits have weakly-developed soils of the Korchea, Savage, and Rhoades types. They are characterized by a thin grayish-brown A horizon. The B horizon is about 0.3 m thick and consists of grayish-brown moderately permeable and slightly alkaline loam with very little calcareous material.
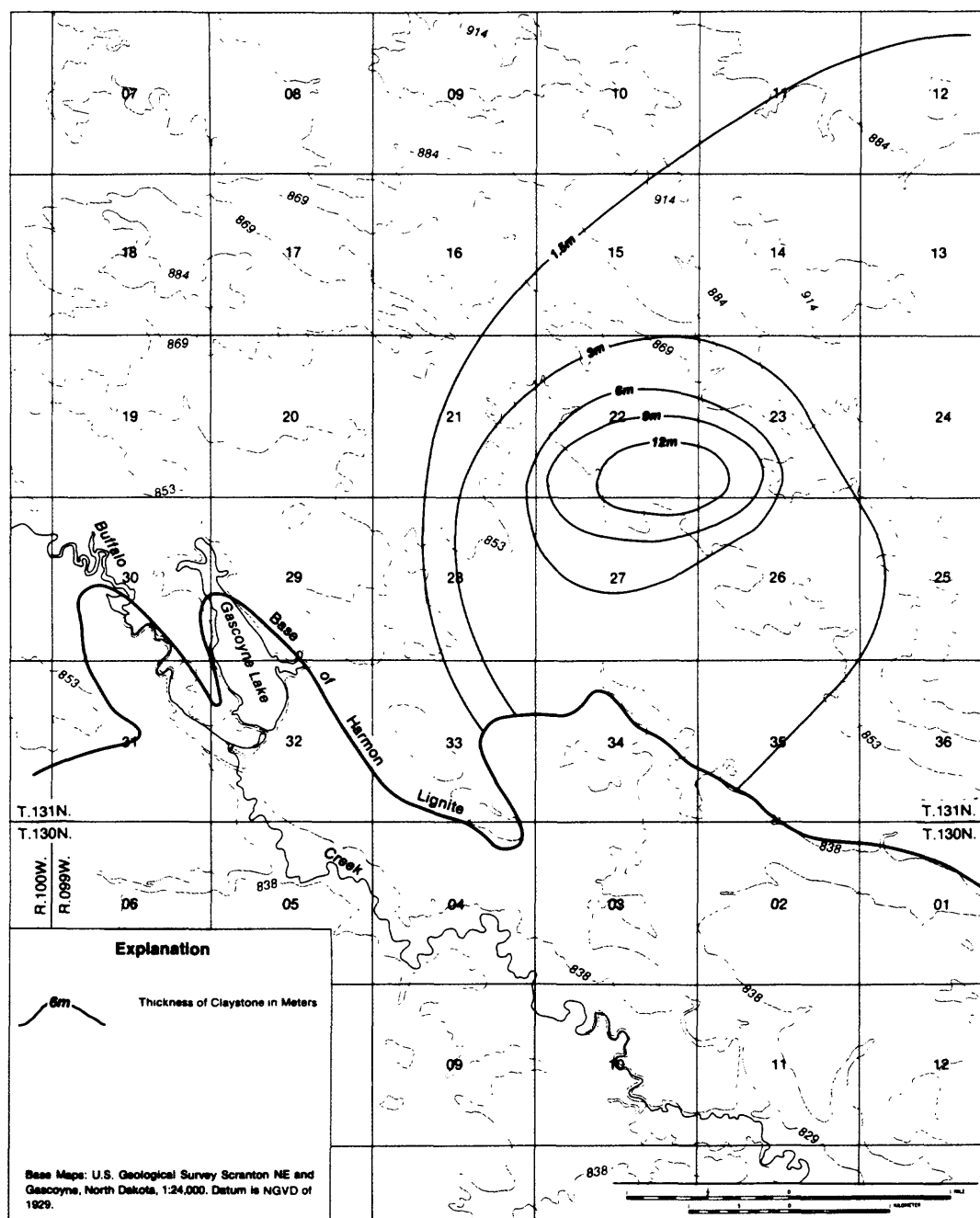
Figure 7. Thickness of claystone bed beneath Harmon lignite

Local precipitation and seepage of surface water north of the mine provide much of the recharge to the shallow Fort Union aquifers in the Gascoyne area. Additional ground water recharge to the southern part of the mine is derived from precipitation on the hilly areas of section 33, T. 131. Nearly impermeable claystones and siltstones of the Cannonball Member minimize groundwater flow into the deeper Fox Hills and Hell Creek aquifers in the study area, thus limiting natural discharge from the shallow aquifers to surface seepage at lower elevations south of the mine.

Basal Tongue River Sandstone Aquifer

North of exposures of the lignite (fig. 5), the Tongue River Member is split into 2 distinct hydrologic units, separated by the impermeable claystone underlying the lignite. South of the lignite outcrop, ground water in the basal Tongue River is unconfined. The line of demarcation between the confined and unconfined basal sandstone runs slightly north of, and roughly parallel to, U.S. Highway 12 in the Gascoyne area.

The potentiometric map (fig. 8) constructed from observation-well data indicates that ground water is discharging to tributaries of Buffalo Creek. Discharge of the major tributary draining the mine area is measured at a gaging station adjacent to a railroad crossing in sec. 03, T. 130.

An obvious feature of the potentiometric contours of figure 8 is the large area of very low gradient centered beneath the mine pits in secs. 26, 27, and 34. The influence of mining operations on the observed potentiometric surface is unclear because of the absence of pre-mining data. However, within the limits of the available data, a relatively flat potentiometric surface in the mine area might be expected from the natural topography (compare the 835 m and 837 m head contours with the 853 m elevation line of figure 4).

A ground water mound (closed 838-meter contour of figure 8) occurs over much of section 33 and part of section 32, where a tongue of the Harmon lignite persists above the water table. Recharge to the basal sandstone at this location must occur by downward percolation of local precipitation.

Hydrographs of wells 130-099-03ABB (H1) and 130-099-01BBB (H2) in the unconfined basal sandstone (fig. 9a) show a pronounced rise in water level during the summer of 1975. The water level rise is presumably due to heavy precipitation and snowmelt in the spring and early summer of 1975. The winter of 1975-76 was relatively warm and dry. The water level rise in H2 during this period was not recorded in H1. Water levels in both wells declined in the summer and fall of 1975 and 1976 because of discharge by evapotranspiration, seepage to streams, and because of the light amount of rainfall.

Only one hydrograph is available for the confined basal sandstone aquifer, from a well located north of the mine at 131-099-22CCB (H3). In the spring of 1975 a lignite pit in the southwest quarter of section 27 T. 131 was extended
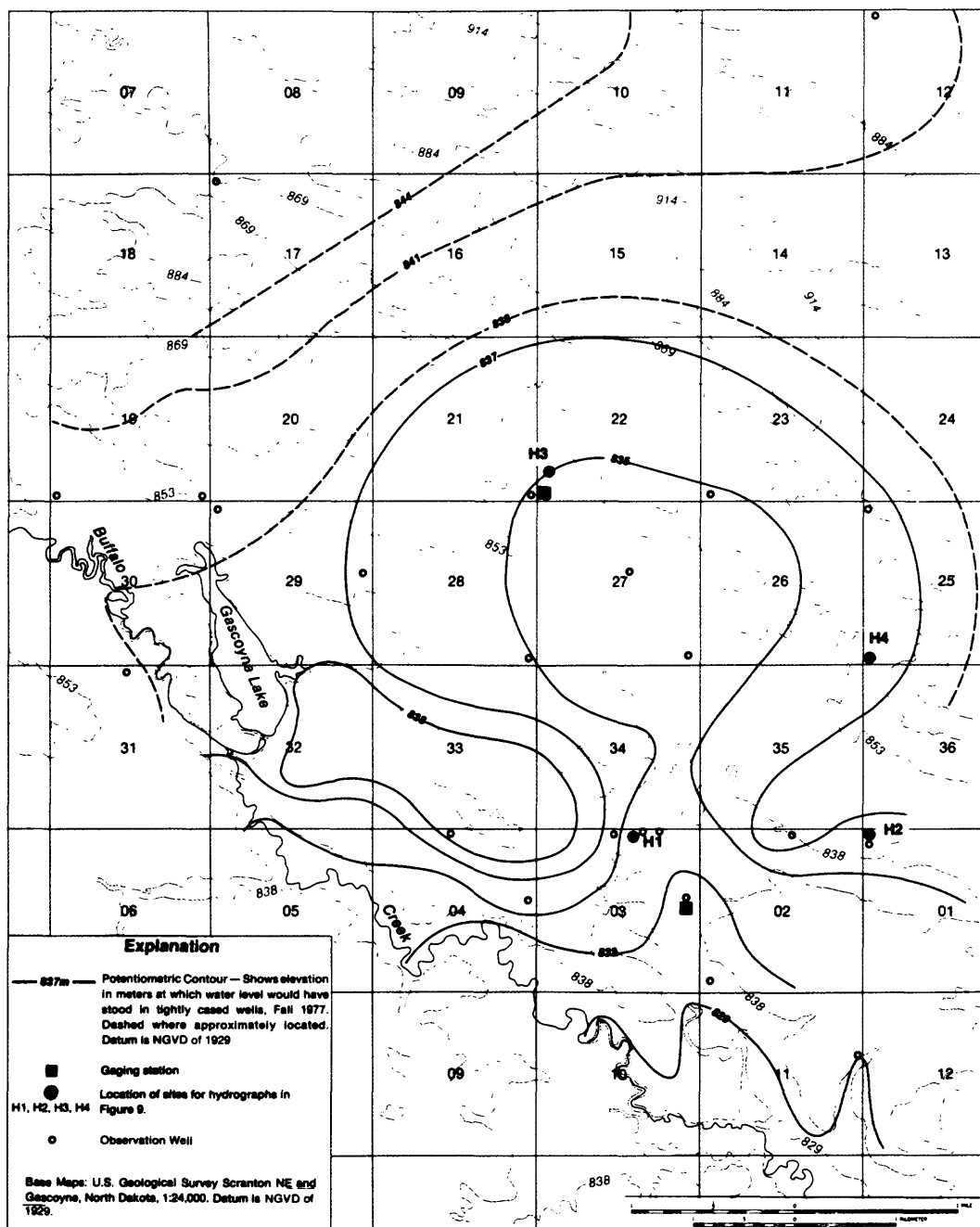
Figure 8. Potentiometric surface in the basal sandstone of the Tongue River Member, Fall 1977
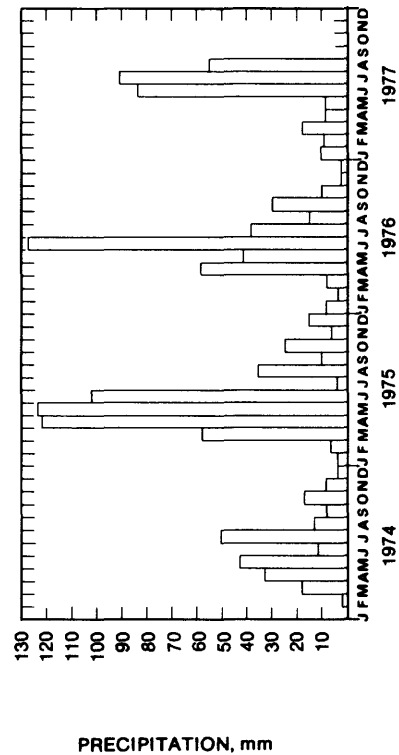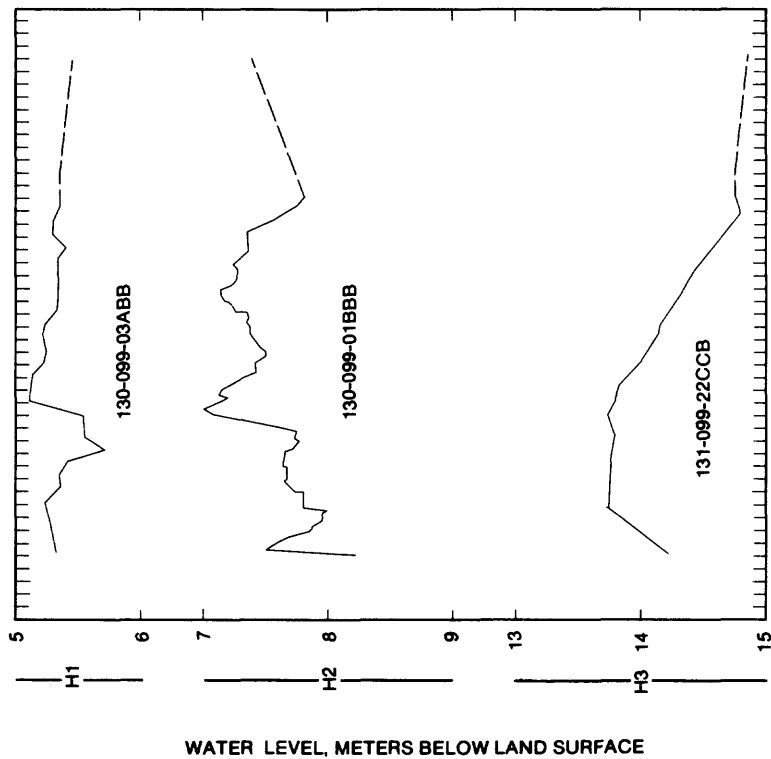
Figure 9. Water-level fluctuations at the Gascoyne lignite mine and precipitation at Hettinger, North Dakota

WATER LEVEL, METERS BELOW LAND SURFACE

PRECIPITATION, mm

-18-

to the northwest corner of the section. The decrease in head recorded by the hydrograph of well 131-099-22CCB (H3) from May 1975 to September 1976 may be the result of increased pumping from the expanded pit.

Harmon Lignite Aquifer

The lignite aquifer is unconfined over most of the study area. In some areas of active mining, the lower part of the lignite is saturated, and the upper part is above the water table. To the north, the lignite lies completely below the water table. A water level map (fig. 10) compiled from observation-well data indicates that the water table in the lignite aquifer generally slopes to the south.

North of the mine, heads in the lignite aquifer are distinctly higher than heads in the basal sandstone, and because the beds dip northeastward, whereas water elevations in both aquifers decrease to the south, recharge to the basal sand in this area must occur by downward leakage through the lignite. South of the mine, the ground-water mound in the unconfined basal sand at sections 32 and 33, T. 131 is recharged by direct infiltration of local precipitation. The area over which flow from the mound dominates the hydrologic system is not well defined. However, comparisons of the potentiometric level maps indicate that heads in the basal sand exceed heads in the lignite over much of section 29, T. 131. Determination of the head relationships between the lignite and the basal sand aquifers is complicated by periodic pumping from the mine pits.

Two major troughs are apparent in the potentiometric surface of the lignite aquifer (fig. 10), one trending northeast-southwest, the other northwest-southeast. The troughs are not the result of seepage to streams because the water level in this area is 9 to 12 m below the stream valleys. The "saddle" between these troughs is at present defined by the head in a single well, located at 131N-099-22DCD. As the head in this well is so important to the configuration of the potentiometric surface (fig. 10), it should be emphasized that this water level has been repeatedly measured over a five-year period. Several samples for chemical and isotopic analysis have been collected from this well, and relative to most wells in the area, it has always pumped exceptionally well. It is obvious, however, that more data in sections 22 and 23, T.131 are needed before the potentiometric surface presented in figure 10 can be accepted as definitive.

The lignite aquifer is recharged primarily by seepage from precipitation and streams. Surface runoff following storms is heavy because the undisturbed overburden materials are fine-grained and the soils are not highly permeable; only a small fraction of the incident precipitation reaches the aquifer. At well 131-099-36BBB2 (H4 in fig. 9B), where the lignite lies below the water table, the hydrograph shows a rise in head in the lignite, presumably due to heavy precipitation and to snowmelt from March 1975 through June 1975. Water level in the well then declined from August 1975 through July 1976 because of evapotranspiration, and because of the small amount of precipitation during that time.

Figure 10.--Potentiometric surface in the Harmon lignite, Fall 1977.

Water in the small Buffalo Creek tributaries and shallow aquifers of the study area is derived entirely from local precipitation. Natural compositions of the ground water should therefore be determined by chemical changes occurring during infiltration of rain or snow melt through the soil zone and unsaturated zone to the water table. The kinds of processes that can alter recharge water chemistry include dissolution of minerals and of products of organic decay, absorption of unsaturated zone gases, cation exchange reactions, redox reactions of solutes with minerals or organic material, and hydrolysis reactions of silicates and aluminosilicates.

North of the mine, recharge to the basal sandstone occurs by downward leakage through the lignite and the underlying confining claystone. Compositions of recharge water reaching the basal sandstone in this area are therefore largely controlled by interactions between solutes in the infiltrating water and reactants in the lignite and claystone. Disruption of the natural pattern of recharge by mining of the lignite would be expected to result in observable changes in the ground-water chemistry of the basal sandstone near active mining areas. In the southern part of the study area, ground water quality in the basal sand is influenced by the ground-water mound centered in section 33, T. 131, by direct infiltration of precipitation at locations where the basal sand is exposed, and by southward-flowing waters in the lignite and the confined sand.

Mineralogy of Overburden, Lignite, and Miscellaneous Surficial Solids

A number of potential sources of recharge-water solutes are evident in the X-ray diffraction data of tables 2A and 3, and in the heavy mineral counts listed in table 2B. Samples for bulk mineralogical analyses and heavy mineral counts were collected from auger and test holes, and from fresh mine cuts. Miscellaneous surface samples were taken from the mine property and from nearby recharge and discharge areas for major mineral identification (table 4).

Mineral data for test well 131-099-23CCC (Table 2A and 2B) are plotted in figure 11 to show the relationship of some important mineral phases to the lignite. At this location the lignite is present from 18 to 29 meters in depth; the present water level is about 22 m below land surface. Before mine dewatering was increased, water level at the site may have been shallower.

The mineral data for well 131-099-23CCC indicate that pyrite and marcasite are scarce above a depth of 12 m and are present in abundance in the coal, particularly the upper part, and in the 5 m of overburden immediately above the lignite. Magnetite and ilmenite grains are common above the lignite, especially near the land surface. Limonite is also an abundant near-surface mineral. Bulk X-ray diffraction analyses show significant amounts of gypsum only at shallow depths. Major quantities of dolomite and considerable amounts of calcite are present in most of the overburden samples. Dolomite persists down to the water table, and reappears at 23 to 26 m.

Depth, m	Gamma log Increasing radiation ⟶	Heavy minerals (frequency per 100 grains)			Bulk x-ray (weight percent)		
		Pyrite/ marcasite	Magnetite/ ilmenite	Limonite	Calcite	Dolomite	Gypsum
		<1	16	34	2	2	1
		—	43	26	0	2	5
		1	2	92	0	7	3
6—		<1	3	59	4	11	2
		—	12	65	0	0	0
		—	5	67	2	8	1
		1	11	67	3	8	0
12—		—	1	5	8	16	0
		3	2	7	8	14	0
		6	2	12	8	12	0
		15	3	9	2	8	0
18—		84	—	2	6	15	0
		84	—	9	0	14	0
		82	—	12	0	3	0
		74	1	14	0	0	0
24—		63	—	29	0	2	0
		46	1	3	0	5	0
		39	2	15	0	0	0
		27	5	3	0	0	0
30—		22	<1	1	0	0	0
		11	—	1	0	0	0
36—							

Gamma log notations: — — — Approximate water level (1977); Lignite interval

Figure 11. Log of well 131-099-23CCC showing mineralogy of sediments

Table 2A.--X-ray mineralogy of Tongue River samples[1]

Depth in meters	Weight percent										
	Quartz	Potassium feldspar	Plagioclase feldspar	Calcite	Dolomite	Gypsum	Chlorite + kaolinite	Illite	Smectite	Mixed layer clay minerals	Total
0-1.5	35	6	6	2	2	1	8	14	14	10	98
1.5-3.0	23	4	2	0	2	5	10	14	7	19	86
3.0-4.6	31	3	3	0	7	3	13	28	3	10	101
4.6-6.1	31	4	4	4	11	2	9	18	3	13	99
6.1-7.6	33	4	2	0	0	0	12	27	4	14	95
7.6-9.1	33	4	4	2	8	1	12	22	3	12	102
9.1-11	31	4	4	3	8	0	11	22r	1	11	96
11-12	26	4	3	8	16	0	7	17	2	4	86
12-14	29	4	3	8	14	0	10	19	2	4	93
14-15	29	3	3	8	12	0	11	14	2	8	91
15-17	29	3	2	2	8	0	11	19	2	17	93
17-18	28	3	2	6	15	0	10	15	1	9	90
18-20	29	3	2	0	14	0	11	22	4	5	87
20-21	32	0	0	0	3	0	12	23	2	22	96
21-23	36	5	3	0	0	0	18	19	1	18	101
23-24	18	2	0	0	2	0	14	15	1	13	3 65
24-26	33	3	1	0	5	0	14	21	1	10	3 88
26-27	12	0	0	0	0	0	9	11	0	9	3 41
27-29	46	6	2	0	0	0	32	16	0	6	108
29-30	44	6	3	0	0	0	16	15	3	8	95
30.5-31.2	52	0	0	0	0	0	14	16	3	6	3 91
31.2-31.6	61	0	0	0	0	0	17	5	0	5	88
31.6-31.9	54	5	3	0	0	0	31	6	2	3	104
33.5-33.8	45	7	7	0	0	0	17	4	8	0	88
55.8-56.1	29	19	0	0	0	0	2	0	25	6	81
56.1-56.4	32	17	4	0	0	0	3	0	28	2	86

[2] Core from test well at 131-099-23CCC (The Harmon Lignite occurs at depths of 20 to 30 m)

Table 2A.--(Continued)

						Weight percent					Mixed layer	
Depth in meters	Quartz	Potassium feldspar	Plagioclase feldspar	Calcite	Dolomite	Gypsum	Chlorite + kaolinite	Illite	Smectite	clay minerals	Total
[2]High wall at 131-099-27BBB (The top of the Harmon Lignite occurs below 7.5 m)											
0-.3	37	6	8	4	3	0	5	9	18	12	102
.3-1.1	36	5	6	5	5	0	5	8	12	10	92
1.1-1.5	46	8	9	6	3	0	2	4	7	8	93
1.5-1.8	40	8	8	8	4	0	4	8	9	7	96
1.8-2.3	41	5	5	5	18	0	11	12	1	4	102
2.3-2.7	37	4	5	4	19	0	9	19	4	4	105
2.7-3.4	44	6	6	4	18	0	10	8	1	2	98
3.4-3.7	38	5	5	5	21	0	10	12	1	2	99
3.7-4.0	37	4	3	2	19	0	10	17	2	7	101
4.0-4.4	44	7	6	2	22	0	12	8	0	0	101
4.4-4.9	46	6	4	0	24	0	11	7	1	3	101
4.9-5.2	45	7	3	0	0	0	14	18	4	13	104
5.2-5.5	39	4	3	0	19	0	12	10	1	6	94
5.5-6.1	44	7	4	0	32	0	12	10	1	0	109
6.1-6.7	43	5	4	0	23	0	13	17	0	2	97
6.7-7.3	45	7	0	0	28	0	15	10	2	2	109
[4]Leonardite pit at 131-099-33DCD (Samples are of leonardite)											
0-.3	4	0	0	0	0	13	0	0	0	0	—[5]
.3-.6	8	0	0	0	0	9	0	0	0	0	—[5]
.6-.9	1	0	0	0	0	21	0	0	0	0	—[5]
.9-1.2	1	0	0	0	0	11	0	0	0	0	—[5]
1.2-1.5	0	0	0	0	0	2	0	0	0	0	—[5]
1.5-2.1	2	0	0	0	0	4	0	0	0	0	—[5]

1 Analysis by U.S.G.S. Water Resources Division analytical laboratory.
2 For heavy mineral counts for these samples see Table 2B.
3 Contains amorphous material.
4 This pit has now been backfilled and the topsoil replaced.
5 Remainder of samples are amorphous material.

Table 2B—Three hundred grain count of heavy minerals from samples of Table 2A[1/]

Depth (m)	Weight percent heavy minerals	Number frequency per 100 grains																												
		Pyrite/marcasite	Magnetite/ilmenite	Hematite	Rutile	Limonite	Leucoxene	Anhedral carbonate	Subhedral carbonate	Apatite	Muscovite	Biotite	Chlorite	Amphiboles	Green hornblende	Brown hornblende	Pyroxenes	Tourmaline	Zoisite	Clinozoisite	Epidote	Staurolite	Garnet	Zircon	Corundum	Beryl	Sphene	Highly altered mineral fragments	Unidentified
											Test well at 131-099-23CCC																		
0–1.5	0.98	<1	16	0	1	34	2	0	0	<1(?)	<1	1	1	1	1	0	0	2	0	0	1	1	13	1	0	<1	5	10	2
1.5–3.0	7.42	0	43	0	<1	26	<1	<1	19	0	1	0	<1	<1	0	0	0	<1	0	0	1	0	2	0	0	0	0	7	0
3.0–4.6	7.95	1	2	0	0	92	0	0	1	0	<1	0	0	0	0	0	0	0	<1	0	<1	0	0	0	0	0	0	2	1
4.6–6.1	4.92	<1	3	0	0	59	<1	0	29	0	1	1	0	<1	0	0	0	0	1	0	<1	0	<1	<1	0	0	0	6	0
6.1–7.6	2.63	0	12	0	0	65	0	0	11	0	0	1	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	10	0
7.6–9.1	1.91	0	5	0	0	67	0	0	20	0	1	0	0	0	0	0	0	2	0	0	0	0	2	0	0	0	0	5	0
9.1–11	3.36	1	11	0	0	67	0	0	17	0	0	1	0	0	0	0	0	0	0	0	0	0	<1	0	0	0	0	3	0
11–12	9.72	0	1	0	0	5	0	81	6	0	<1	0	0	0	0	0	0	0	0	<1	<1	0	0	0	0	0	0	6	0
12–14	2.06	3	2	0	0	7	<1	20	50	0	2	<1	0	0	<1	0	0	1	0	<1	<1	0	2	0	<1	0	0	11	0
14–15	1.56	6	2	0	0	12	0	36	23	0	6	1	0	0	0	0	0	<1	<1	<1	0	0	2	0	0	0	0	12	0
15–17	2.75	15	3	0	0	9	0	31	15	0	0	<1	0	0	<1	0	<1	<1(?)	0	0	<1(?)	0	16	0	0	0	0	8	<1
17–18	24.76	84	0	0	0	2	0	8	3	0	0	0	0	0	0	0	0	<1	0	0	0	0	0	0	0	0	0	2	<1
18–20	21.66	84	0	0	0	9	0	5	3	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	<1	0	0
20–21	12.32	82	0	0	<1	12	0	1	3	0	0	0	0	0	0	0	0	0	0	0	0	0	<1	0	0	0	0	1	0
21–23	4.94	74	1	0	0	14	0	<1	7	0	0	0	0	0	0	0	0	<1	0	0	<1	0	<1	0	0	0	0	3	0
23–24	.85	63	0	0	0	29	0	0	5	0	0	<1	0	0	0	0	<1	0	0	<1	0	0	<1	<1	0	0	0	1	0
24–26	4.09	46	1	0	<1(?)	3	0	1	7	0	0	1	0	0	1	0	0	0	0	0	<1	0	1	0	0	0	0	4	<1
26–27	.16	39	2	0	0	15	0	1	22	0	0	0	0	0	0	4	<1	<1	<1(?)	0	1(?)	0	1	1	0	0	0	13	0
27–29	2.23	27	5	0	<1(?)	3	0	0	13	0	34	8	0	0	0	0	0	<1	1	0	<1	0	1	0	0	0	0	6	0
29–30	3.44	22	<1	0	0	1	<1	0	9	0	37	16	0	0	0	0	0	0	3	0	0	0	0	0	0	0	0	12	0
30–31	2/—	11	0	0	0	1	0	0	8	0	45	24	0	0	0	0	0	<1	0	0	0	0	0	0	0	0	0	11	0

Table 2B--(Continued)

Number frequency per 100 grains

Depth (m)	Weight percent heavy minerals	Pyrite/marcasite	Magnetite/Ilmenite	Hematite	Rutile	Limonite	Leucoxene	Anhedral carbonate	Subhedral carbonate	Apatite	Muscovite	Biotite	Chlorite	Amphiboles	Green hornblende	Brown hornblende	Pyroxenes	Tourmaline	Zoisite	Clinozoisite	Epidote	Staurolite	Garnet	Zircon	Corundum	Beryl	Sphene	Highly altered mineral fragments	Unidentified
0-.3	1.65	0	8	5	0	33	0	0	32	0	1	<1	0	1	0	<1	1	<1	1	1	1	1	6	0	0	0	1	7	<1
.3-1.1	3.58	1	5	0	0	32	<1	1	50	0	2	<1	0	0	0	1	1	<1	1	0	2	0	1	<1	0	0	<1	3	<1
1.1-1.5	8.76	0	6	2	0	50	0	0	26	0	3	<1	0	0	0	<1	1	0	0	1	1	0	2	1	0	0	0	4	0
1.5-1.8	4.11	0	6	3	<1	36	0	2	31	0	3	2	0	0	0	<1	1	1	0	0	1	0	4	1	0	0	0	8	<1
1.8-2.3	18.03	2	1	0	0	32	0	0	51	0	8	1	0	0	0	0	0	1	0	0	0	0	0	0.	0	0	0	4	<1
2.3-2.7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2.7-3.4	12.33	0	1	0	0	1	0	0	86	0	5	1	0	0	0	1	<1	<1	0	0	0	0	1	0	0	0	0	4	<1
3.4-3.7	15.31	0	1	0	0	0	0	1	81	0	9	1	0	0	0	0	0	1	4	0	0	0	0	0	0	0	0	2	0
3.7-4.0	12.6	1	4	0	0	2	0	<1	77	0	12	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0
4.0-4.4	9.13	0	0	0	0	<1	1	0	87	0	4	2	0	0	0	1	0	1	1	0	0	0	0	0	0	0	0	2	0
4.4-4.9	14.3	0	0	0	0	0	0	0	91	0	6	2	0	0	0	0	0	<1	0	0	0	0	0	<1	0	0	0	1	0
4.9-5.2	33.21	65	1	0	0	3	0	0	15	0	15	0	0	0	0	0	0	0	0	0	0	0	<1	0	0	0	0	<1	0
5.2-5.5	6.6	67	<1	0	0	2	0	0	15	0	14	<1	0	0	0	0	0	0	<1	0	0	0	<1	0	0	0	0	0	0
5.5-6.1	8.86	15	0	0	0	2	<1	0	64	0	11	3	0	0	<1	1	0	1	0	0	0	0	<1	0	0	0	0	3	0
6.1-6.7	8.82	14	0	0	0	<1	0	0	74	0	9	1	0	0	0	0	<1	<1	<1	0	0	0	0	0	0	0	0	1	1
6.7-7.3	3.96	30	0	0	0	<1	<1	<1	37	0	21	8	0	0	<1(?)	0	0	<1	0	0	0	0	2	0	0	0	0	<1	0

1/ Analyses by U.S.G.S. Water Resources Division analytical laboratory.
2/ -- No data.

Table 3.—X-ray diffraction analyses of Tongue River samples above and below the Harmon Lignite[1]

Weight percent

Depth in meters	Quartz	Potassium feldspar	Plagioclase feldspar	Calcite	Dolomite	Gypsum	Pyrite	Siderite	Chlorite + Kaolinite	Illite	Smectite
[2]Core from test hole at 130-099-11ADD (This location is stratigraphically below the Harmon Lignite)											
1.5	40	10	0	0	20	10	0	0	15	15	0
3.0	35	5	tr	tr	25	10	0	tr	15	15	0
5.2	50	5	tr	0	0	0	0	0	20	15	15
7.0	30	0	5	0	20	tr	0	3	5	10	35
8.8	30	5	5	10	15	0	0	tr	5	5	30
11	30	0	0	0	0	10	10	tr	5	5	45
13	35	5	tr	tr	0	tr	0	0	10	20	35
16	35	15	tr	0	tr	0	0	tr	5	10	25
18	35	tr	10	0	20	0	0	0	20	10	10
20	20	20	5	0	10	0	tr	0	10	10	20
Core from test hole at 131-99-21CCB (The Harmon Lignite occurs at depths of 18 to 29 m)											
1.5	60	15	tr	5	tr	tr	tr	0	10	10	tr
3.0	55	tr	5	15	15	0	0	0	tr	10	tr
4.6	55	tr	5	5	20	3	0	0	10	10	10
6.1	50	5	5	5	20	tr	tr	tr	10	15	5
9.8	30	5	5	15	20	0	0	0	5	10	10
13	40	10	0	15	20	5	0	tr	10	10	tr
15	40	0	10	10	20	5	10	0	15	15	tr
16	30	10	tr	10	20	10	10	0	15	15	0
18	60	tr	0	0	0	0	tr	tr	tr	15	tr
25.5	60	tr	0	0	0	0	tr	tr	5	25	5

Table 3.--(Continued)

				Weight percent							
Depth in meters	Quartz	Potassium feldspar	Plagioclase feldspar	Calcite	Dolomite	Gypsum	Pyrite	Siderite	Chlorite + Kaolinite	Illite	Smectite
[3]Samples from highwall at 131-99-28BBB (The top of the Harmon Lignite occurs at 12 m)											
.6	35	tr	0	0	tr	15	0	0	20	15	20
1.8	30	tr	0	0	tr	15	0	tr	15	25	tr
3.4	30	tr	5	10	20	0	0	tr	15	15	tr
5.2	40	5	tr	15	20	0	0	tr	10	20	tr
6.7	35	0	0	10	20	0	0	0	15	15	tr
8.2	45	0	0	0	15	tr	0	tr	20	15	0
9.5	40	0	0	0	20	0	0	0	20	20	0
10	40	0	0	tr	20	0	0	0	20	20	tr
11	40	0	0	tr	0	20	0	0	15	15	tr
12[4]	0	0	0	0	0	85	15	0	0	0	0
[3]Samples from highwall at 131-99-28CCC (The top of the Harmon Lignite occurs at 11 m)											
1.5	40	tr	0	0	0	tr	0	0	15	15	35
2.4	60	10	0	0	0	0	tr	0	tr	25	tr
6.1	50	tr	tr	10	20	0	tr	tr	5	5	tr
7.6	40	tr	tr	0	25	5	0	0	15	15	0
[3]Sample from highwall at 131-99-29BBB (The top of the Harmon Lignite occurs at 3 m)											
1.5	35	tr	0	0	20	10	tr	0	15	20	tr
[3]Samples from highwall at 131-99-29CBB (The top of the Harmon Lignite occurs at 2.4 m)											
1.2	100	tr	0	0	0	0	0	0	0	0	0
2.4	35	tr	0	0	20	5	0	tr	15	20	tr

Table 3.--(Continued)

	Weight percent										
Depth in meters	Quartz	Potassium feldspar	Plagioclase feldspar	Calcite	Dolomite	Gypsum	Pyrite	Siderite	Chlorite + Kaolinite	Illite	Smectite
Core from test hole at 131-99-33DCD (The Harmon Lignite occurs at depths of 9-17 m)											
1.5	50	tr	0	0	15	0	0	tr	15	15	tr
3.0	45	5	tr	0	15	0	0	tr	15	15	0
5.2	30	10	0	0	20	tr	0	tr	15	20	10
7.9	30	tr	0	0	20	15	0	tr	15	15	10
16	30	5	0	0	tr	tr	tr	0	30	15	15
18	50	10	0	0	0	0	0	0	20	15	tr
22	40	5	10	0	10	0	0	tr	20	15	5
25	35	5	tr	0	15	0	0	5	15	15	15
[3]Samples from highwall at 131-99-34AA (The top of the Harmon Lignite occurs at 6.1 m)											
1.2	50	5	0	0	0	15	0	0	15	20	tr
2.4	35	10	5	5	30	0	0	tr	15	15	10
3.7	45	5	tr	tr	35	0	0	0	10	5	5
5.2	50	tr	0	0	30	tr	0	0	10	5	tr

[1] Analyses by David R. Pheasant, Geodurma, Inc., Dallas, Texas.
[2] tr: minerals are present in amounts less than 5%.
[3] Depths are approximate.
[4] Sample from top of Harmon Lignite.
[5] Sample from clay bed within lignite.

Table 4.—X-ray diffraction analyses of miscellaneous samples from the vicinity of Gascoyne, North Dakota[1]

Sample	Sampling Date	Source or Location	Major identifiable minerals
Center of massive sulfide concretion	7/08/77	Highwall at 131-99-28BBB	Pyrite, quartz, dolomite
Massive sulfide concretion Center	7/08/77	Highwall at 131-99-28BBB	Pyrite, quartz, marcasite, dolomite, clay
Weathered rim			Quartz, dolomite, kaolinite or chlorite illite
Weathered concretion Gray material around hollow center	7/03/77	Surface of spoils at 131-99-34BAB	Quartz, gypsum, illite, kaolinite or chlorite
Outer iron-stained mass			Quartz, gypsum, illite, kaolinite
Crystals forming on surface of brine	8/22/78	Small puddle at 130-99-02ADA	Mirabilite
Crusted surface soil	8/22/78	Near brine puddle	Quartz, thenardite, bloedite, dolomite, calcite, soda syngenite, 10Å clay
Evaporites	8/22/78	Near brine puddle	Thenardite, bloedite, quartz, soda syngenite
Surface soil	8/22/78	Near ponded water at 130-99-01ACC	Bloedite, quartz, thenardite, gypsum, soda syngenite
Evaporites	5/27/79	In a ditch along road at 131-99-10CBB (elev. ~ 900 m)	Quartz, hexahydrite, bloedite, thenardite, dolomite, gypsum, 7Å clay, 10Å clay, 14Å clay (including mixed-layer clays), plagioclase feldspar

[1] Analysis by Ruth Deike, USGS, Reston, VA.

Available X-ray diffraction data for the other sites in the vicinity of the mine (tables 2A and 3) indicate abundant dolomite in sediments over most of the Gascoyne area. In several of the vertical profiles, dolomite decreases abruptly below the water table. Calcite is generally less abundant than dolomite, and is not found at all in core samples from well 131-099-33DCD. Gypsum is present in significant amounts at depths slightly above the lignite in samples from T.131, sections 21,28,29, and 33, and in leonardite from section 33. Small amounts of siderite were found in many of the sediment samples.

Beds of massive concretions were observed a few meters above the Harmon lignite at several fresh mine cuts. The concretions are usually 2 to 10 cm in diameter, with dense, lustrous centers and gray surfaces. X-ray diffraction analyses of samples of two of these nodules (table 4) show that the cores are largely pyrite, dolomite, and quartz, with considerable marcasite in one of the samples.

Concretions are also abundant in the mine spoils at Gascoyne. They resemble the pyrite nodules in surface appearance; however, they are much lighter, with little or no pyrite remaining in the cores. The weathered concretion (table 4) from spoils at T.131, section 34BAB was hollow; the only identifiable sulfur-containing mineral in this concretion is gypsum, and no carbonate minerals were detected. Hand-lens inspection of fine-grained soil from leveled spoils in section 34 suggests that gypsum is abundant on the surface of reclaimed spoils.

Gypsum and other sulfate minerals are also found at the surface of sites unaffected by the present mining activity. During the summer months, numerous evaporite crusts are observed in roadside ditches and in marshy places throughout the higher elevations north of the mine. In nearly every instance, remnants of lignite and either weathered concretions or marked iron staining can be seen on the banks of road cuts above the crusts. A sample of an evaporite was scraped from a ditch at 131-099-10CBB, in the hills that supply recharge to the shallow aquifers near Gascoyne. Results of X-ray diffraction analysis (table 4) show that this material contains major amounts of gypsum and of highly soluble sodium and magnesium sulfates. Similar sulfate minerals are found in evaporites from the low-lying fields south of the mine, below the present outcrop of the Harmon lignite.

Cation Exchange Properties and Soil Extract Compositions

Cation exchange capacities and exchangeable cations were determined on a number of samples from the Gascoyne area. In addition, saturation extract determinations were provided for some samples by Fred Sandoval, U.S. Department of Agriculture, Agricultural Research Station, Mandan, North Dakota (Table 5). The saturation extract data refer to distilled water-saturated soil samples in contact with air; analyses were made on water removed from the soil paste by suction filtration. The analyzed extract concentrations approximate saturated conditions in a well-aerated soil environment. Methods used for these determinations are described in Sandoval and Power (1977). Disparities are evident in the cation exchange capacity values found by different methods for the test well at 131-099-23CCC. Much better agreement was obtained for the other samples.

Table 5.—Cation exchange capacity, exchangeable cations, and saturation extracts, Gascoyne lignite mine, North Dakota

Depth meters	Cation exchange capacity (meq/100 g)		Exchangeable cations[1] (meq/100g)				Saturation extracts[2] (meq/L)						
	DEN[3]	NDSL[4]	Na	K	Ca	Mg	Ca	Mg	Na	CO3	HCO3	Cl	SO4
Test well 131-099-23CCC													
0-1.5	2.7	27	8.0	0.45	9.0	10	20.7	56.7	85.1	0	1.2	0.1	161
1.5-3.0	5 —	21	4.35	.42	8.0	14	20.1	66.3	93.5	0	.8	<.1	179
3.0-4.6	3.2	6.2	2.71	.45	4.0	4.0	21.0	38.1	66.9	0	.6	<.1	125
4.6-6.1	2.3	8.9	.74	.19	4.0	4.0	21.0	37.2	62.0	0	.5	<.1	119
6.1-7.6	2.6	24	.31	.05	21	7.0	17.8	25.4	33.5	0	1.0	<.1	76
7.6-9.1	—	9.5	.60	.22	5.4	3.5	13.0	17.8	25.5	0	1.1	.1	55
9.1-11	—	12	.97	.27	6.0	6.0	19.6	27.6	38.4	0	1.0	.1	84
11-12	2.9	14	1.14	.21	8.0	6.5	10.3	13.6	21.5	0	2.2	.1	43
12-14	—	8.8	.42	.18	5.0	3.5	7.9	10.0	21.3	0	2.3	.1	37
14-15	—	5.3	.20	.15	2.0	3.3	5.9	6.8	21.1	0	2.7	.1	31
15-17	—	11	.36	.30	8.0	3.0	3.2	3.6	19.7	0	2.2	.1	25
17-18	2.5	26	2.74	.35	15.0	9.0	6.6	6.7	25.8	0	1.9	.1	37
18-20	22	17	2.18	.27	6.0	12.0	2.4	2.5	28.1	0	4.7	.1	28
20-21	69	32	3.74	.31	15	13	5.0	5.3	53.5	0	12.2	.1	52
21-23	74	33	3.68	.26	16	13	1.7	1.7	33.4	0	8.5	.1	28
23-24	81	41	4.47	.25	22	14	6.0	6.0	68.4	0	16.5	.2	63
24-26	73	—	—	—	—	—	5.5	6.1	73.6	0	18.6	.2	66
26-27	81	—	—	—	—	—	3.4	3.6	56.5	0	13.4	.1	70
27-29	50	—	—	—	—	—	1.4	1.4	31.5	0	5.6	.1	28
29-30	67	—	—	—	—	—	1.0	1.0	27.3	0	5.1	<.1	24
30-31	70	—	—	—	—	—	12.0	1.3	84.3	0	13.4	.3	90
High wall at 131-099-27BBB													
0-.3	19	14	.31	.09	7.0	6.5	1.4	3.4	4.2	0	3.9	.1	5
.3-.6	14	41	—	—	—	—	10.0	18.7	8.2	0	2.0	.1	35
.6-1.1	11	18	.05	0	7.0	11	6.1	26.3	13.8	Trace	2.0	.4	43
1.1-1.5	9.1	10	.18	.03	7.5	4.0	10.1	52.2	25.0	Trace	1.9	.8	85
1.5-1.8	4.0	3.5	.26	.04	2.5	1.0	18.6	96.2	33.2	0	.4	2.4	145
1.8-2.3	9.2	8.6	.16	.02	5.4	3.0	15.2	32.4	15.5	0	1.0	1.6	60
2.3-2.7	3.2	1.8	.06	.10	2.8	.8	21.6	36.1	12.4	0	.8	1.6	68
2.7-3.4	4.3	4.5	.10	.06	2.1	2.1	17.0	18.3	9.1	0	1.3	.4	42
3.4-3.7	6.2	2.3	.09	.09	1.5	.5	12.6	11.0	4.7	0	1.4	.2	26
3.7-4.0	2.3	3.2	.39	0	1.4	.5	17.5	20.6	9.9	0	.7	.8	46
4.0-4.4	2.7	2.0	.01	.01	1.7	.9	18.7	18.9	13.2	0	1.0	.4	50
4.4-4.9	9.8	7.3	.06	.07	6.9	.8	3.9	3.9	4.4	0	1.4	.1	11
4.9-5.2	5.5	3.5	.04	.06	2.5	3.5	8.5	9.0	10.8	0	2.2	.1	26
5.2-5.5	2.4	2.9	.04	.02	1.6	1.2	16.4	15.6	9.3	0	.3	.2	40
5.5-6.7	2.0	2.3	.50	.04	.5	2.5	18.2	58.0	35.9	0	1.1	1.4	109
6.7-7.3	3.5	4.2	.30	.05	6.0	5.0	6.5	6.9	21.1	0	.8	.2	34
7.3-8.8	—	—	—	—	—	—	8.9	12.0	49.2	0	11.5	.3	56
Test well 131-099-27DDD													
0-1.5	7.0	12	1.22	.07	7.0	5.0	—	—	—	—	—	—	—
1.5-3.0	6.2	8.0	.28	.10	6.2	2.0	—	—	—	—	—	—	—
3.0-4.6	6.0	7.0	.42	.09	5.2	1.8	—	—	—	—	—	—	—
4.6-6.1	6.8	10	.46	.12	7.1	3.0	—	—	—	—	—	—	—
6.1-7.6	8.3	10	.15	.13	7.5	2.7	—	—	—	—	—	—	—
7.6-9.1	6.4	9.0	.30	.18	7.5	1.7	—	—	—	—	—	—	—

Table 5—(continued)

Depth meters	Cation exchange capacity (meq/100 g)		Exchangeable cations[1] (meq/100g)				Saturation extracts[2] (meq/L)						
	DEN[3]	NDSL[4]	Na	K	Ca	Mg	Ca	Mg	Na	CO_3	HCO_3	Cl	SO_4
Test well 131-099-27DDD (continued)													
9.1-11	10	11	2.47	.01	8.0	.8	—	—	—	—	—	—	—
11-12	62	67	8.7	.09	47	20	—	—	—	—	—	—	—
12-14	37	37	4.3	.17	22	7	—	—	—	—	—	—	—
14-15	42	42	10	.13	21	14	—	—	—	—	—	—	—
15-17	73	73	16	.15	42	18	—	—	—	—	—	—	—
17-18	82	82	21	.11	39	20	—	—	—	—	—	—	—
18-20	39	39	6	.14	24	10	—	—	—	—	—	—	—
20-21	11	12	3.6	.17	6.2	2.5	—	—	—	—	—	—	—
21-23	7.9	11	3.4	.17	8.3	4.2	—	—	—	—	—	—	—
23-24	5.9	7.0	3.1	.14	3.6	2.4	—	—	—	—	—	—	—
24-26	11	12	3.5	.12	6.0	3.8	—	—	—	—	—	—	—
26-27	6.7	12	4.2	.19	5.8	4.0	—	—	—	—	—	—	—
27-29	9.8	12	5.0	.21	6.0	3.0	—	—	—	—	—	—	—
29-30	8.2	11	4.2	.18	5.1	2.5	—	—	—	—	—	—	—
30-32	9.6	10	3.3	.18	5.6	1.8	—	—	—	—	—	—	—
32-34	8.0	8.0	3.0	0	3.0	2.9	—	—	—	—	—	—	—
33-35	13	14	8.4	.43	2.0	6	—	—	—	—	—	—	—
35-37	13	14	8.8	.05	1.8	4.4	—	—	—	—	—	—	—
Test well 130-099-03ABB													
0-1.5	5.3	9.3	.60	.11	7.0	1.0	—	—	—	—	—	—	—
1.5-3.0	6.3	8.4	1.0	.10	3.8	3.1	—	—	—	—	—	—	—
3.0-4.6	6.9	6.6	.70	.15	2.3	3.0	—	—	—	—	—	—	—
4.6-6.1	8.6	9.3	1.4	.24	3.5	3.0	—	—	—	—	—	—	—
6.1-7.6	8.6	11	1.8	.32	5.0	3.7	—	—	—	—	—	—	—
7.6-9.1	8.2	9.2	2.2	.18	4.7	3.5	—	—	—	—	—	—	—
9.1-11	4.9	6.1	1.4	.21	1.7	2.8	—	—	—	—	—	—	—
11-12	2.6	4.7	1.0	.05	1.0	2.5	—	—	—	—	—	—	—
Test well 130-099-03ADC													
0-1.5	25	23	7.2	.48	9.0	8.0	—	—	—	—	—	—	—
1.5-3.0	17	22	14	.19	11	7	—	—	—	—	—	—	—
3.0-4.6	46	38	18	.38	12	9	—	—	—	—	—	—	—
4.6-6.1	44	41	13	.70	20	15	—	—	—	—	—	—	—
6.1-7.6	16	14	3.22	.26	8.9	1.9	—	—	—	—	—	—	—
7.6-8.2	45	48	10	.60	20	20	—	—	—	—	—	—	—
Leonardite pit at 131-099-33DCD													
0- .3	66	—	—	—	—	—	—	—	—	—	—	—	—
.3- .6	62	—	—	—	—	—	—	—	—	—	—	—	—
.6- .9	74	—	—	—	—	—	—	—	—	—	—	—	—
.9-1.2	79	—	—	—	—	—	—	—	—	—	—	—	—
1.2-1.5	79	—	—	—	—	—	—	—	—	—	—	—	—
1.5-2.1	80	—	—	—	—	—	—	—	—	—	—	—	—

[1] Determination by North Dakota State Laboratories using an ammonia-acetate solution. Analysis by Garvin O. Muri.

[2] Data furnished by Fred Sandoval, Agricultural Research Service, Mandan, N. Dak., using methods described by Sandoval and Power (1977).

[3] Determination by U.S. Geological Survey, Denver Central Laboratory, using Cesium 137 (U.S. Geo. Survey Bull. 1140-B).

[4] Determination by North Dakota State Laboratories using an ammonia-acetate solution on a sodium-saturated sample.

[5] — No data.

Test wells 131-099-23CCC and -27DDD penetrate the Harmon lignite at depths of 18-29 m and 11-20 m, respectively (figure 12). The data of table 5 show that cation exchange capacities of samples from these wells are much higher in the lignite than in the overburden. High capacities are also found in leonardite from section 33. Alkaline earth ions exceed sodium ions on exchange sites throughout the vertical intervals tested, except for the 34-37 m zone in the section 27 well. Exchangeable sodium is lowest above the lignite. Relationships between lithology, cation exchange capacity, and exchangeable cations for the -27DDD samples are illustrated in figure 12. Exchangeable alkaline earths also exceed sodium in samples from other sites in the vicinity of the mine (table 5).

Saturation extract data for the test well (table 5) show that extractable sodium and alkaline earth ions are present in roughly equivalent amounts through the upper 12 m of soil. Below this level, calcium and magnesium decrease. Through the lignite interval (18-29 m) at 131-099-23CCC, the saturation extracts are predominantly sodic. No well-defined trends are noted in relative cation levels from the high wall samples at 131-099-27BBB; however, sodium concentrations do increase below a thin lignite seam at 5-6 m, and dissolved sodium is the principal cation in extracts from the 7-9 m interval.

Sulfate is the principal anion in all the saturation extracts. Very high concentrations of extractable sulfate were found in samples from the upper 6 m of the test well at 131-099-23CCC and from the 1.5-1.8 m and 5.5-6.7 m intervals at the high wall site. Significant amounts of bicarbonate are present in extracts from the lignite interval of the test well and in the deepest sample from the high wall. Chloride levels are minor in all the saturation extracts.

Ion-exchange selectivity experiments were made by Mark E. Crawley (formerly Water Resources Division, U.S. Geological Survey, Bismarck, North Dakota) on cuttings from the section 27 test well (Mark E. Crawley, written communication, 1978). Neutral test solutions containing known concentrations of Ca^{2+} and Na^+ were equilibrated for 24 hours with ground ($< 250\mu m$) samples of sediments from the lignite interval and from deeper clay and sand horizons at the site. The mixtures were then filtered through $0.45\mu m$ membrane filters, and the filtrates were analyzed for Ca^{2+} and Na^+. Crawley found that, for a 0.2 to 6.3 range of initial mol ratios of calcium to sodium, dissolved Ca decreased and dissolved sodium increased as a result of the experiments, indicating a strong preference for calcium over sodium on cation-exchange sites in all of the sediment samples tested.

Lignite Composition

Leonardite from section 33, T. 131 and 2 samples of the Harmon lignite from a fresh mine cut in section 28 were collected for chemical analyses. The fuel-grade samples were from separate lignite seams divided by a 0.3 m clay parting. At the time of sampling, continuous pumping was required to remove water from the base of the mine pit; water seeping from the clay parting indicated that the lower lignite seam was completely saturated under pre-mining conditions at this site.
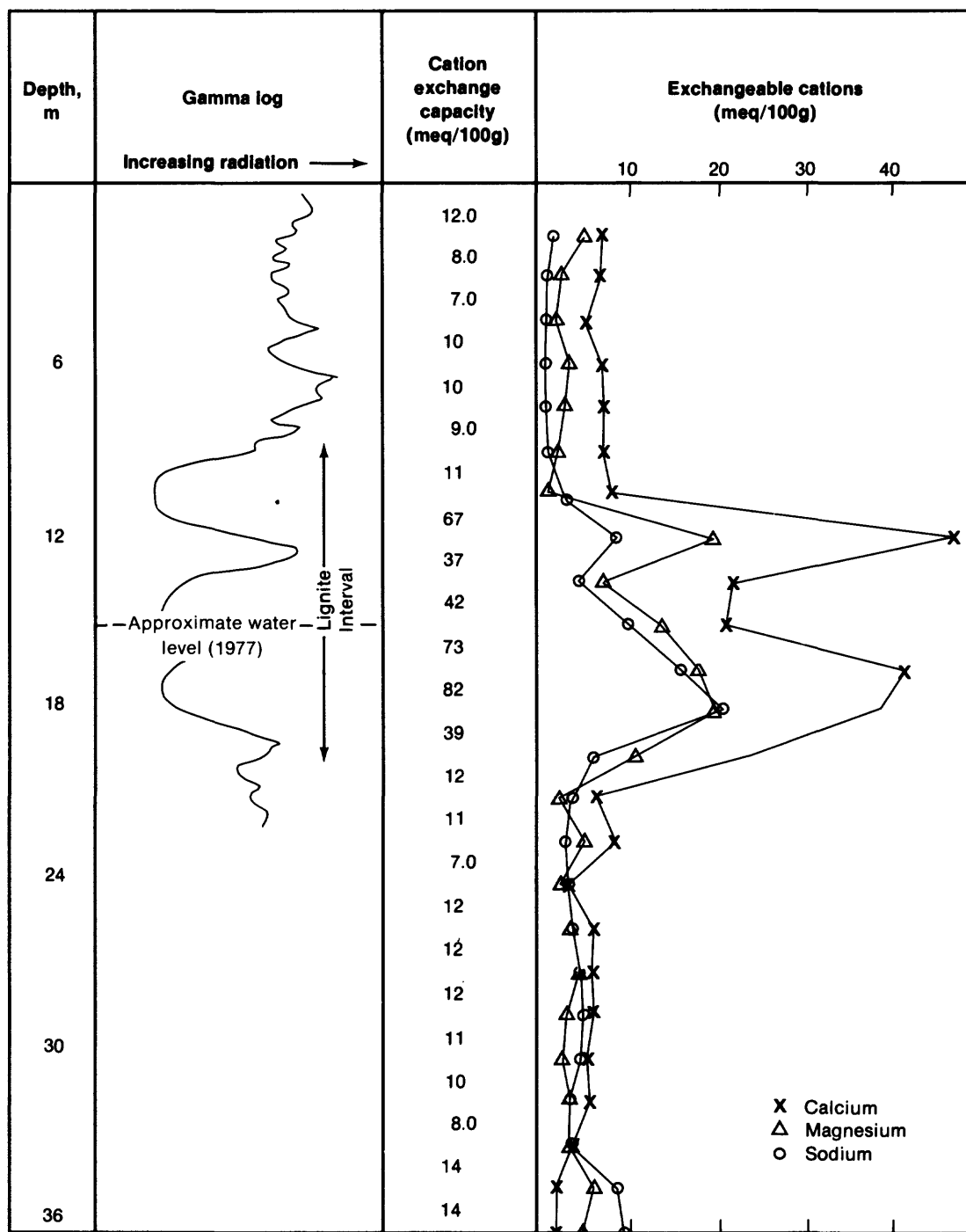
Figure 12. Log of well 131-09902-27DDD showing cation exchange capacity and concentrations of exchangeable cations

Results of ultimate, sulfur-species, and ash analyses of the coal samples are listed in table 6. Values for the ultimate analyses were calculated from "as received" determinations after taking into account the moisture and ash contents - (determined on separate samples of the coal). Ultimate analyses for the leonardite and upper lignite seam are nearly identical to ultimate compositions of coal humic acid (Schnitzer and Khan, 1972, p. 31). The deeper sample is significantly higher in carbon and hydrogen, and lower in oxygen, than are the more weathered leonardite and upper lignite. Also, sulfate-sulfur is very low in the saturated bottom seam, but constitutes a significant proportion of the total sulfur in the leonardite and the upper seam. Apparently the natural environment below water table is chemically more reducing than that in the upper lignite bed at the section 28 site. If the small (molecular) amounts of nitrogen and sulfur are ignored, then the proportions of carbon, hydrogen, and oxygen correspond to hypothetical compounds with formulas roughly $C_3H_{2.5}O$ and C_5H_5O for the upper and lower lignite beds, respectively. The formal valence of carbon in the upper seam is, accordingly, - 1/6, whereas that in the lower seam is - 3/5, compared to a zero value for simple carbohydrates of composition $C_n(H_2O)_m$.

Compositions of ash from the Gascoyne lignite are shown in table 6B. Levels of most of the major ash components are greatest in the bottom seam; iron is an exception. Molecular ratios of calcium to magnesium, calculated from the data, are nearly uniform at about 2.1 for the 3 samples. Ash content of the alkali metals is low relative to the alkaline earths. Relatively large amounts of sulfur and small quantities of chloride and fluoride are retained in the ash of each of the samples.

Laboratory leaching experiments were conducted to determine the availability of halides in the coal to infiltrating water. Results of the tests are listed in Table 6. Samples of lignite were shaken overnight with deionized water, then filtered through 0.45 μm membrane filters. Chloride determined in the filtrates amounted to .0024%, .0050%, and .0022% by weight of the leonardite, upper seam, and lower seam samples, respectively. Corresponding fluoride percentages in the leachates were .0002, .0003, and .0004. If most of the halides originally present in the coal are retained during the ashing process, then comparisons of the leaching experiment results with the ash compositions (table 6B) indicate that much of the chloride and a few tenths of a percent of the fluoride present in the lignite can be removed by infiltrating water.

Surface Discharge from the Mine Area

The mine area is drained by a tributary of Buffalo Creek. Discharge is measured above and below the mine. The drainage system is well integrated, with only two or three small natural lakes and several small stock ponds above the mine area, and several ponds on the mine property. Total drainage area above the stream-gaging station at 130-99-03ADD is about 40 km^2. Flow of the tributary is extremely variable; monthly mean discharge varied from zero to more than 0.55 m^3/s (fig. 13) during the period of study. The discharge measured below the mine at times included mine pumpage, as part of the pumpage is discharged into the Buffalo Creek tributary (the rest of the mine pumpage is discharged into Gascoyne Lake and into closed basins). Peak discharge during the period of record was in April and May 1975.

Table 6.--Composition of Harmon lignite and leonardite from Gascoyne, N.D. mine

6A. Ultimate and sulfur-species analyses [1]

Sample	Ultimate analyses, % by weight on a water- and ash-free basis					Sulfur-species analyses, % by weight on an as-received basis		
	H	C	N	O	S	Sulfate-S	Pyritic-S	Organic-S
Leonardite	4.6	64.1	1.2	28.7	1.2	.17	.16	.37
Upper seam	4.2	64.1	1.3	28.3	2.1	.67	.14	.33
Lower seam	5.9	71.3	1.1	20.2	1.4	.01	.21	.54

6B. Ash compositions, % by weight on a whole coal basis [2]
[Ashed at 525°C.]

Sample	Si	Al	Ca	Mg	Fe	Na	K	Mn	Cl	F	S -
Leonardite	.61	.20	.53	.15	.28	.04	.03	.02	.004	.09	.21
Upper seam	.37	.18	.62	.18	.27	.04	.01	.05	.005	.04	.56
Lower seam	.98	.45	1.69	.46	.14	.26	.02	.2	.006	.07	.86

[1] Analyses by U.S. Bureau of Mines, Coal Analysis Section, Pittsburgh, PA.
[2] Analyses by U.S. Geological Survey, Branch of Coal Resources, Reston, VA.
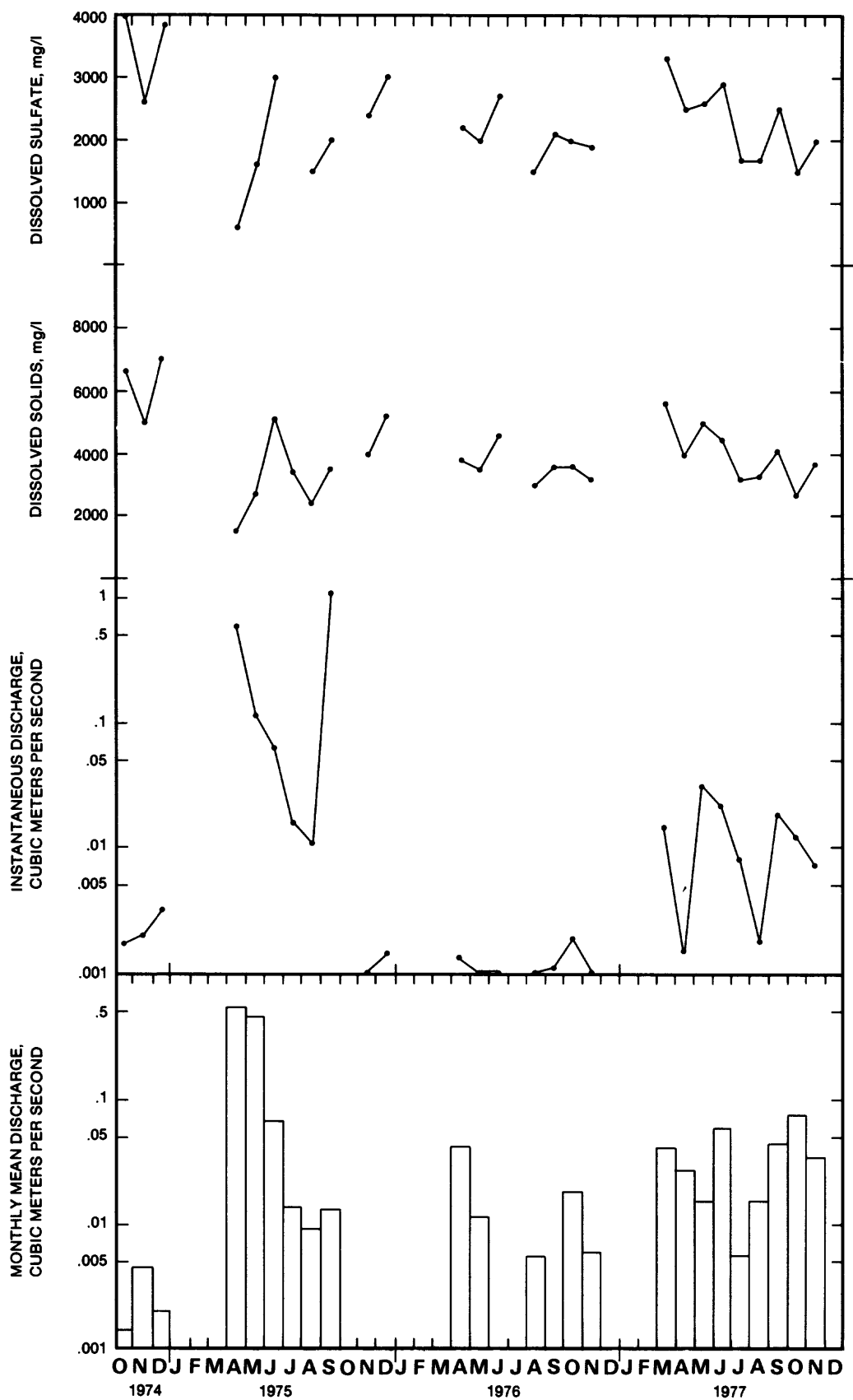
Figure 13. Discharge and water quality at Buffalo Creek tributary below Gascoyne mine (06355310)

A number of water samples were collected from the tributary stream below the mine during the 3-year period from Oct. 1974 to Nov. 1977. Results of sulfate and dissolved solids analyses of these samples, and correlative instantaneous discharge measurements, are plotted on fig. 13. Good correlation between total dissolved solids and sulfate, the major anion, is evident in the plots. An inverse relationship between sulfate and discharge, which would be indicative of high-sulfate ground water and low-sulfate surface water components of the stream, is not apparent in the data of figure 13 except during a period of very high flow in the spring of 1975.

In 1977 and early spring of 1978, water quality samples were collected from Buffalo Creek about 13 km west of Gascoyne, and from the tributary stream above and below the mine. Stream discharge and sulfate concentration data are listed in table 7. The diluting effect of heavy spring runoff is apparent in the 1978 data. Also, Buffalo Creek water upstream from Gascoyne is in general much lower in sulfate than is the tributary stream water. Comparison of data from the two tributary stream stations indicates that sulfate concentrations are generally higher at the downstream site; however, sulfate levels are also high above the mine (greater than 1000 mg/L during periods of low flow).

Gases in the Unsaturated Zone

Sampling nests devised by Weeks (1978) (fig. 14) were installed at selected sites at and near the mine to collect soil gases at various heights above the water table. A downstream vacuum pump, with an intake valve to limit gas flow rate, was used to draw soil gas up into sampling containers. The system is pumped for several minutes to exhaust atmospheric air from the samplers and from the piezometer pipe, then the sampler and gas well are isolated from the pump by closing the intake valve. Samples are collected when the well pressure, measured by a vacuum gage in the sampling line, recovers to the atmospheric value.

Chemical compositions of the soil gases were determined by gas-solid chromatography (Hobba and others, 1977). Results of analyses of sequential samples from three different gas probes, collected after various pumping times (table 8A), indicate that the sampling procedure is generally satisfactory; major variations in composition at a single site were found only in the sample which contained liquid water. Interpretation of results (table 8B) from several of the gas probes is complicated by the occasional presence of perched ground water at sampling depth. In these instances, the collected sample may not be representative of the undisturbed soil gas phase because of differences in solubilities of the various gases in water.

Results of isotopic analyses of some soil gases also are listed in table 8B. Samples for the ^{13}C and ^{18}O analyses were collected in evacuated stainless steel cylinders with basically the same pumping procedure used to obtain the chemical composition samples. Carbon dioxide gas from these samples was isolated in the laboratory, and carbon and oxygen isotopes in the CO_2 were analyzed by mass spectrometry.

Table 7.—Discharge and sulfate concentration data for surface-water
stations near Gascoyne, North Dakota

Collection Date	Buffalo Creek nr. Buffalo Springs 06355250 [1]		Buffalo Cr. Tributary above mine 06355308 [1]		Buffalo Cr. Tributary below mine 06355310 [1]	
	Discharge m^3/sec	Sulfate mg/L	Discharge m^3/sec	Sulfate mg/L	Discharge m^3/sec	Sulfate mg/L
3-01-77	[2] --	--	--	--	.0045	3300
3-09-77	.0156	420	--	--	--	--
4-05-77	--	--	.0003	2700	.0156	2300
4-08-77	.0040	330	--	--	--	--
6-01-77	--	--	.0003	1800	.0311	2900
10-04-77	--	--	.0003	1400	.0181	1600
3-23-78	--	--	.280	350	--	--
3-24-78	--	--	.170	120	--	--
3-29-78	[3]	20	.142	190	--	--
4-05-78	--	--	[3]	420	--	--
4-06-78	--	--	--	--	.130	730
4-07-78	[3]	80	[3]	75	--	--

[1] U.S. Geological Survey, Water Resources Division station number.
[2] -- No data.
[3] Discharge high; not measured.
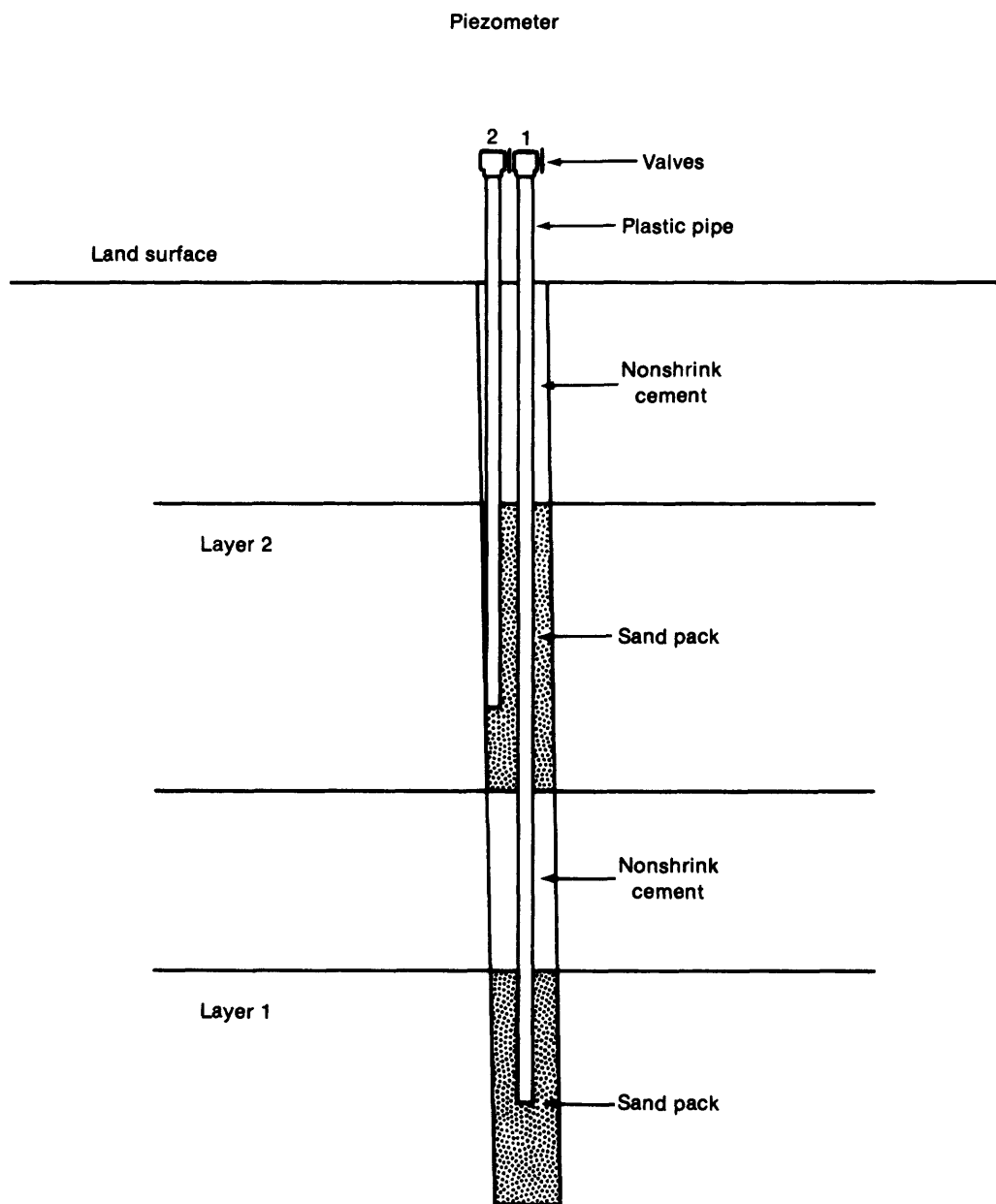
Figure 14. Typical construction of soil-gas piezometer

Table 8A.--Unsaturated zone gas compositions, sequential samples, June 1976

[Pumping rate approximately .03m^3/min. (1 ft.^{3}/min.)]

Site Location	Probe depth (meters)	Pumping time, min.	Percent by volume [1]			
			N_2	O_2	Ar	CO_2
131-099-36BCC	13.7	5	80.7	.03	1.16	18.1
		15	80.6	.02	1.15	18.2
		60	80.7	.02	1.14	18.2
131-099-35BDB	8.8	5	87.6	.05	1.22	11.1
		60	87.0	.43	1.24	11.3
131-099-34BAC	6.1	5	77.1	.02	1.11	21.7
		15	77.0	.01	1.11	21.9
		60 [2]	72.8	.05	1.07	26.1

[1] Ideal gas behavior assumed; values determined as % of measured total sample pressure, normalized to (sum of analyzed gases = 100%).
[2] This sample contained liquid water.

Table 8B. Results of chemical and isotopic analyses of unsaturated-zone gases from the vicinity of Gascoyne, North Dakota

Location	Probe depth (m)	Gas composition, % by volume[a]					Isotope analyses of CO_2 gas				
		Sampled Mo./Yr.	N_2	O_2	Ar	CO_2	Sampled Mo./Yr.	$\delta^{13}C$[b]	$\delta^{18}O$[c]	Sampled Mo./Yr.	^{14}C[d] % Modern
130-099-11ADD	1.2	6/77	78	20.0	1.0	.28	6/77	-22.8	+28.3		
	e4.9	e6/77	e81	e18.0	e1.1	e.02	e6/77	e-4.8	e+21.2		
	4.9						e7/77	e-12.6	e+19.0		
	1.2	8/78	77	22.0	1.0	.27					
	1.2	8/80	77	22.0	1.0	.18					
	f4.9	f8/80	f79	f7.2	f1.0	f13.0					
131-099-21CCB	3.0	7/77	82	15.0	1.1	1.6	6/77	-22.7	+21.9		
	5.8	7/77	79	18.0	1.1	1.3	6/77	-19.6	+26.5		
	5.8	7/77	80	18.0	1.0	1.2					
	8.5	7/77	79	19.0	1.0	.95	6/77	-17.2	+26.3		
	g12.2	g7/77	g79	g16.0	g1.2	g2.9					
	g14.6	g7/77	g87	g12.0	g1.2	g<.01					
	3.0	8/78	78	19.0	1.0	2.3	8/78	-22.4			
	5.8	8/78	79	19.0	1.0	1.4	8/78	-20.4			
	8.5	8/78	80	18.0	1.0	1.1	8/78	-17.8			
	3.0	5/79	81	17.0	1.1	1.1	5/79	-24.2		5/79	114.0
	5.8	5/79	80	17.0	1.0	1.3	5/79	-21.8		5/79	91.0
	8.5	5/79	80	18.0	1.0	1.0	5/79	-18.5		5/79	51.0
	3.0	8/80	77	20.0	1.0	2.0					
	5.8	8/80	77	20.0	1.0	1.7					
	8.5	8/80	78	20.0	1.0	1.2					
131-099-33DCD	2.7	6/77	79	19.0	1.0	.73	6/77	-20.9	+26.0		
	h5.8	h6/77	h79	h19.0	h1.0	h1.2	6/77	-23.8	+25.0		
	5.8	7/77	79	18.0	1.0	1.4					
	9.1	6/77	81	.2	1.1	18.0	6/77	-23.3	+25.1	7/77	2.4
	12.8	6/77	82	.2	1.1	18.0	6/77	-22.9	+25.2		
	e,g14.9	e,g6/77	e,g78	e,g21.0	e,g1.2	e,g.10					
	5.8	8/78	79	15.0	1.1	4.9	8/78	-22.2			
	9.1	8/78	81	.06	1.1	18.0	8/78	-23.2			
	12.8	8/78	81	.06	1.1	18.0					
	2.7	5/79	79	19.0	1.1	.44				5/79	103.0
	h5.8	h5/79	h79	h14.0	h1.0	h5.6				5/79	10.0
	19.1	i5/79	i81	i1.9	i1.1	i16.0				5/79	1.8
	j12.8	j5/79	j82	j.3	j1.1	j17.0				5/79	2.2
	2.7	8/80	77	21.0	1.0	.92					
	h5.8	h8/80	h74	h20.0	h1.0	h5.4					
	9.1	8/80	80	.09	1.1	19.0					
	12.8	8/80	80	.06	1.1	19.0					

Table 8B.—Continued

Location	Probe depth (m)	Gas composition, % by volume					Isotope analyses of CO_2 gas				
		Sampled Mo./Yr.	N2	O2	Ar	CO2	Sampled Mo./Yr.	δ13C	δ18O	Sampled Mo./Yr.	14C %Modern
131-099-34BAC	1.2	9/76	77	11.0	1.0	11.0					
	3.4	9/76	73	1.0	1.0	25.0					
	6.1	9/76	74	.3	1.0	25.0					
	1.2	7/77	77	9.5	1.0	12.0	6/77	-12.0	+25.6	7/77	20.6
	3.4	7/77	79	.6	1.1	19.0	6/77	-11.7	+25.6	7/77	12.2
	e6.1	e7/77	e80	e.03	e1.1	e19.0				7/77	13.2
	1.2	8/80	79	16.0	1.0	4.4					
	3.4	8/80	84	3.5	1.1	12.0					
131-099-35BDB	2.7	9/76	83	10.0	1.1	5.5					
	5.8	9/76	87	6.2	1.1	5.8					
	e8.8	e9/76	e88	e.10	e1.2	e11.0					
	2.7	6/77	79	14.0	1.0	6.4	6/77	-21.6	+28.7	7/77	18.1
	5.8	6/77	79	12.0	1.1	7.9	6/77	-21.6	+24.4		
	2.7	8/80	77	15.0	1.0	6.7					
	5.8	8/80	78	13.0	1.0	8.4					
	8.8	8/80	87	.08	1.2	12.0					
131-099-36BCC	3.0	9/76	97	1.8	1.3	.06					
	e5.2	e9/76	e82	e17.0	e1.1	e.56					
	g,h7.6	g,h9/76	g,h93	g,h.9	g,h1.2	g,h4.8					
	10.9	9/76	82	.06	1.4	16.0					
	13.7	9/76	80	.04	1.1	19.0					
	e3.0	e6/77	e78	e21.0	e1.0	e.08	6/77	-34.1	+32.6		
	e5.2	e6/77	e90	e1.4	e1.9	e7.0					
	e,g,k7.6	e,g,k6/77	e,g,k78	e,g,k19.0	e,g,k1.0	e,g,k1.2	6/77	-27.3	+31.4	7/77	2.1
	10.9	6/77	80	.3	1.1	18.0	6/77	-17.7	+23.6	7/77	2.1
	13.7	6/77	81	4.2	1.1	13.0	6/77	-17.3	+28.6		
	3.0	8/80	77	11.0	1.0	11.0					
	10.9	8/80	79	3.2	1.0	17.0					
	e13.7	e8/80	e77	e21.0	e1.0	e1.6					

a Ideal gas behavior assumed; values determined as % of total sample, normalized to (sum of analyzed gases) = 100%.
b Reported values in parts per mille (0/00) relative to the PDB standard.
c Reported values in parts per mille (0/00) relative to the SMOW standard.
d Samples collected in 1977 analyzed by Radioisotope Laboratory, U.S. Geological Survey, Water Resources Division, Reston, Virginia; later samples analyzed by H. Haas, Radiocarbon Laboratory, Southern Methodist University, Dallas, Texas.
e Liquid water in the sample.
f .05% nitrous oxide in the sample.
g Well pressure recovered very slowly after pumping.
h .01% nitrous oxide in the sample.
i .01% methane in the sample.
j .08% methane in the sample.
k Trace of nitrous oxide in the sample.

For the ^{14}C analyses, a peristaltic pump was used to pull soil gas through a sampling flask containing a CO_2 absorbing solution. Ammoniacal strontium chloride solution was the CO_2 absorbent for the 1977 sample; a sodium hydroxide-strontium chloride solution was used for the more recent ^{14}C samples (see Haas and others, 1983, for further details).

Gas probes in the nest at 130-099-11ADD are screened in the basal sandstone. Compositions of the soil gas at the 1.2 m depth are quite close to atmospheric levels except for some enrichment in carbon dioxide. CO_2 levels of a few tenths of a percent are common in shallow soil zone environments, and the $\delta^{13}C$ of -22.8‰ in the 1977 sample indicates an organic carbon source (probably root respiration and plant decay) for the CO_2. Less negative $\delta^{13}C$ values determined for two samples from the 4.9 m probe indicate a substantial component of inorganically-derived CO_2 in the unsaturated zone at this depth. Major differences in O_2 and CO_2 levels between the 1977 and 1980 samples from 4.9 m are evident in the data of table 8B. Infiltration of precipitation during the Spring of 1977 possibly contributed to the unusually low CO_2 at 4.9 m by dissolving much of the accumulated unsaturated-zone content of this gas. Nitrous oxide in the later sample demonstrates the occurrence of denitrification near the 4.9 m probe during the dry 1980 summer.

The gas sampling probes at 131-099-21CCB are located above the Harmon lignite, which is below water table at this location. Moderate percentages of CO_2 and some depletion of atmospheric oxygen are observed in unsaturated-zone gases from this site. The $\delta^{13}C$ values suggest a predominantly organic origin for CO_2 in the gases, with an increasing inorganic component at increasing depths. Pressures recovered very slowly after exhausting air from the casings of the 12.2 and 14.6 m probes at this site. Gas samples were collected several hours after pumping was stopped; pressures had not recovered to the atmospheric value at the time of sampling.

High CO_2, low O_2 unsaturated-zone gases were obtained from 9.1 m and 12.8 m probes at the 131-099-33DCD site. The probes are screened in a weathered remnant of the Harmon lignite. Carbon isotope analyses indicate that the carbon source for much of the CO_2 at these depths is old (2.4 percent modern carbon) and almost entirely organic. Undoubtedly continuing reaction of atmospheric oxygen with the lignite is generating the high-CO_2 unsaturated-zone gas at this site.

Two gas sampling sites are in reclaimed spoils on the mine property (131-099-34BAC and -35BDB). High-CO_2, low-O_2 gases also are found in the unsaturated zone at these locations. [14]C results indicate that significant amounts of modern carbon are present in CO_2 from these wells. $\delta^{13}C$ data suggest that the carbon source is largely organic at the section 35 site, and roughly half inorganic in CO_2 from the section 34 wells. A decrease in CO_2 concentration with time is evident from the data of table 8B for the gases from section 34; on the other hand, CO_2 has increased slightly since 1976 in the unsaturated zone at the section 35 site. At the deep section 36 gas probes, (above the lignite and beneath a persistent zone of perched water at the 5.2 m probe and an impermeable clay-rich bed at about 7.6 m), the unsaturated zone CO_2 levels exceeded 10 percent and oxygen was depleted in the 1976 and 1977 samples. Carbon isotope

analyses of these deep samples indicated a largely organic ($\delta^{13}C$ = -17) and old (% modern carbon = 2.1) carbon source. By 1980, however, major changes had taken place in the unsaturated-zone gas compositions at this site. At the deepest probe, oxygen level was equal to the atmospheric value, and CO_2 had decreased to less than 2%; a significant amount of oxygen was present at the 10.9 m probe, and the CO_2 concentration at the shallowest probe had increased greatly over the 1977 value. It was noted that only small amounts of water were collected by pumping the 5.2 m probe in 1980, suggesting depletion of the perched water body, by evaporation or by downward migration. Removal of this barrier to unsaturated-zone movement of gases probably led to the observed profound changes in the vertical profile of gas compositions.

Quality of surface waters and unsaturated-zone waters

Water quality samples were collected from streams, ponds, and the unsaturated subsurface in the vicinity of the mine. Results of chemical analyses of these waters are listed in table 9. Stream samples include one from the Buffalo Creek tributary at the gaging station below the mine, and one from a small stream draining a marsh at the base of hills east of the mine. The latter stream joins the Buffalo Creek tributary between the mine property and the gaging station; the area drained by the small stream at the samping point lies entirely upstream of the Harmon lignite.

Both stream waters are highly mineralized. Comparison of the chemical compositions of the two samples indicates that water derived from the mine is higher in pH, alkalinity, sulfate, chloride, and sodium, and lower in alkaline earth cations, than water draining higher elevations east of the mine.

The ponded waters collected in township 130 are from a marshy area south of, and stratigraphically below, the present outcrop of the Harmon lignite. A thin soil covers the basal sandstone unit in this area. A surface sheet of mirabilite ($Na_2SO_4 \cdot 10H_2O$) was present on the brine puddle when the sample from section 02 was collected. Sulfate, fluoride, potassium, strontium, magnesium, and sodium concentrations in this brine are extremely high, as they are in water from the pond at section 01ACC.

Sodium-magnesium sulfate evaporites (mineralogic analyses in table 4) covered the ground surface just above the ponded water at section 01. The widespread occurrence of the "popcorn" textured evaporitic deposits in topographically low-lying areas south of the mine—most obvious in sections 1 and 2, township 130-implies evaporative concentration of standing water to the point of saturation with highly soluble salts. This degree of mineralization of rain water or snowmelt would require extreme evaporative concentration. Less extreme evaporation would be required if the water subject to evaporation were initially a relatively high-sulfate ground water, rather than rain water. A ground-water source for the ponded water is likely—the water table is very near land surface in this area. Equivalents of sulfate in the three ponded waters from Township 130 are approximately balanced by sodium plus magnesium. Mol ratios of Ca/Mg are < 0.5, and decrease with increasing total solute concentrations; presumably gypsum and/or calcium carbonate minerals are deposited early as evaporation proceeds.

Table 9. Results of chemical analysis of surface waters and unsaturated-zone waters from the vicinity of Gascoyne, North Dakota

Location	Source	Collected Mo./Yr.	Depth below land surface (m)	pH	Titration alkalinity (meq/L)	Sulfate (mg/L)	Chloride (mg/L)	Fluoride (mg/L)	Silica (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Strontium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Mol ratio Ca/Mg
Flowing waters															
1/ 130-099-03ADD	Stream draining mine--below mine	10/74		8.2	14.6	3400	16	1.2	7.3	210	140	2/--	1400	13	.91
36CCD	Stream draining marsh east of mine--above lignite	8/78		7.3	8.5	2600	5.0	3.0	5.5	350	230	7.8	490	20	.92
Ponded surface waters															
130-099-01ACC	Over unconfined basal ss	8/78		7.8	45.6	54000	150	27	16	760	4500	23	16700	310	.10
01BCB	Over unconfined basal ss	8/78		7.9	12.6	3800	9.4	6.0	9.6	260	370	6.2	1230	21	.43
02ADA	Over unconfined basal ss	8/78		8.0	49.2	230000	164	64	8.8	550	20000	54	68000	410	.02
131-099-34CCB	Over unconfined basal ss	8/78		7.9	5.7	1600	7.2	1.4	.0	140	230	3.9	450	5.5	.37
Perched ground waters															
130-099-11ADD	Flooded gas probe --in unconfined basal ss	See note3/	4.9	8.2	3.5	7200	44	1.4	6.6	170	140	1.3	1960	22	.74
1/ 12BCC	Lysimeter--in unconfined basal ss	5/78	4.9	5.3	.11	11000	97	.3	17	460	980	--	3200	22	.28
131-099-26DDD	Lysimeter--above lignite	5/78	6.1	7.1	23.6	16000	80	.5	13	100	890	--	6500	46	.07
28CCC	Seep from highwall --above lignite	7/77	7.6	7.9	4.3	5200	139	1.5	6.5	430	800	.7	590	15	.33
1/ 33DCD	Lysimeter--in upper part of lignite	5/78	10.4	6.8	10.3	3200	8.9	.1	27	560	340	--	550	26	1.00
36BCC	Flooded gas probe --above lignite	6/77	5.2	7.9	9.0	8200	7.0	3.0	13	160	870	3.6	2100	26	.11

1/ Analyses by USGS Water Resources Division Central Laboratories; other analyses by J.C. Chemerys, USGS Water Resources Division, Reston, VA.
2/ -- No data.
3/ Analytical values are means of 2 samples, collected July 1977 and August 1978.

Concentrations of dissolved solutes in the shallow pond at section 34, township 131 are much lower than those in the ponded waters in township 130. No evaporite crusts were observed along the margins of this pond. The principal source of water to the pond presumably is local precipitation. The unusually low silica value may indicate a biological silica removal process in this pond.

Perched ground waters were collected from soil gas probes, from lysimeters, and from a seep on the high wall at a fresh mine cut. Major solute levels in these waters are less than the values determined for the highly concentrated surface waters; nevertheless, sulfate concentrations in the perched waters exceed 3000 mg/L (table 9). Chloride concentrations > 40 mg/L in four of the perched waters suggest evaporative concentration of the unsaturated-zone waters. Simple dissolution of gypsum, calcite, and dolomite in dilute recharge water would yield a ground water with molar concentrations of calcium greater than magnesium. However, Ca/Mg mol ratios of the perched waters are ≤ 1, despite the presence of gypsum and calcite along with dolomite in much of the shallow overburden in the Gascoyne area (tables 2A and 3). Evidently selective removal of calcium from the aqueous phase occurs in the shallow unsaturated zone.

Ground-Water Quality

During the period of this study, a number of observation wells on and near the lignite mine were sampled repeatedly in an effort to identify temporal changes in ground-water quality which might be attributed to the mining operations. Sulfate concentrations of the samples are listed in table 10. Mean annual values are reported for wells which were sampled more than once in a particular year. The data are divided into 4 groups: A) wells screened in the Harmon lignite; B) wells screened in the confined basal sandstone under- lying the lignite; C) wells screened in the unconfined basal sandstone; and D) wells in the basal sandstone which yield water of unusually high pH (pH > 10 in at least two of the samples collected from each of the sites).

The data of table 10 indicate that sulfate concentration increased in the lignite aquifer well 21CCB1 over the 5-year period 1976-81. Dewatering of the section 28 mine pit less than 1 km to the south may have influenced water qual- ity of this well by increasing the local ground-water flow and inducing recharge from a higher-sulfate source. Erratic temporal changes in sulfate levels at lignite well 22DCD could be caused by mine pumpage from the section 27 pit. The 4-year trend of increasing sulfate in the unconfined sandstone well 33DAD2 may be associated with up-gradient leonardite mining, and changes in some other wells might also result from mine operations. However, other explanations must be sought to account for the substantial variations in ground-water sulfate con- centrations in the wells that are hydraulically and geographically removed from the mining activity, and that comprise the majority of the wells sampled in this study.

The procedure used to obtain samples for water quality analyses may be inappropriate for some of the Gascoyne area wells. Ordinarily, water quality samples are collected only after removing standing water from the well casing

Table 10. **Sulfate concentrations in ground waters from the vicinity of Gascoyne, North Dakota**

Location	1974	1975	1976	1977	1978	1979	1980	1981
				Year				
		Sulfate concentrations, milligrams per liter						
A. Wells screened in the Harmon lignite								
131-099-21CCB1			290	330			400	420
131-099-22DCD			1800	1900	2100	2200	1800	2000
131-099-23CCC2			660				710	
131-099-26ADA			940			1100		860
131-099-26DDD2		310	300	300				
B. Wells screened in the confined basal sandstone								
131-099-17BBB2			93				73	
131-099-19CCC	1300		1300					1500
131-099-21DDD	570	510	490					
131-099-23CCC1		890	160				79	
131-099-27DDD1			200	160				
131-099-29ADD1		490	420					510
131-099-29BBB	280	280	310					270
131-099-36BBB1	140	180	200					
C. Wells screened in the unconfined basal sandstone								
130-099-01BBB	870	1200	1100		2200			
130-099-02CCC2			720	830				1100
130-099-03ADD			3400		1500			3400
130-099-03BAA		3000						4400
130-099-04ADD2			4800			4500		5100
130-099-04BAA			2100	2200	2200			
131-099-31BAA		1000						1000
131-099-32DBC		750	780					
131-099-33CCC	1600	1600	1600					
131-099-33DAD2		6000	6500	7400	7500			
131-099-34ACC1	960	930	910					
131-099-34BCA	3300	3800	3800					
D. High pH wells in the basal sandstone								
130-099-02ABB			120					100
130-099-03AAB1		50	120					260
131-099-33BAA1			320					140
131-099-33BAA2			1400					700

and allowing the readily-monitored parameters (usually temperature, pH, and electrical conductivity) to stabilize with continued pumping. However, the Fort Union sands and silts are fine-grained, and are interbedded with numerous thin clay and lignite seams. Interbedding can impede flow and vertical mixing in the aquifer unit under undisturbed conditions. In this environment, well yields from short screened intervals are often very low. Continuous pumping produces rapid drawdown, which in turn may accelerate mixing of the water at screen depth with induced recharge, possibly of a different chemical composition, from overlying strata. The resulting sample may thus represent a composite of waters from several horizons in the aquifer, with a composition which may vary with rate and duration of pumping. In such low-yield wells it is impossible to judge whether samples have been withdrawn by lateral flow at screen depth or have a significant component of vertical mixing.

Vertical mixing probably accounts for the marked changes in well 130-099-01BBB, east of the mine and removed from the effects of mining operations. During the August 1978 sampling, water level in this 10-cm-diameter well was lowered 3 m after pumping 25 liters at a rate of 0.6 liters per minute. An additional 30 liters were discharged to waste, then the well was allowed to recover overnight. The following day, after further pumping and collection of a water quality sample, a sudden color change was observed in the effluent water. The observation prompted collection of a second sample. Results of chemical analyses (table 11) show that the two samples are quite different chemically; for this pair, as well as for two samples collected on successive days in November 1974, the second samples are lower in alkalinity, higher in silica, and much higher in sulfate and major cations than are the earlier samples from each pair. Admixture of induced recharge (calculated composition in table 11) with the 11/20/74 sample and the first 8/27/78 sample in proportions of 19% and 50% respectively, can account for most of the observed changes in the ground water composition. The calculated recharge composition is qualitatively like that of the perched ground water from 131-099-36BCC a kilometer to the north (table 9). Calcium, magnesium, and sodium are evidently higher in the recharge than in the formation water at the well screen depth; however, the proportions of these cations in the recharge apparently changed between 1974 and 1978, so that the mixing ratios of .19 and .50 do not apply to these constituents. The steady decline in chloride levels at well 01BBB may reflect gradual removal of some local contamination introduced during well construction in 1974. An irregular trend toward the earlier 1974 values is observed in the data (table 11) for most of the dissolved species in the interval from November 1974 through August 1978.

Results of chemical analyses of ground waters from wells and lysimeters that were set below the water table in the Gascoyne area are listed in table 12A. The data are divided into five groups: 1) Lysimeters and wells screened in the upper 4 m of the water table above the Harmon lignite or in the unconfined basal sand; 2) wells screened in the Harmon lignite; 3) wells in the confined basal sandstone beneath the lignite; 4) wells in the unconfined basal sandstone; and 5) wells (in the basal sandstone) which yield water of unusually high pH. Bicarbonate, carbonate, and hydroxide equivalents were combined and are listed as titration alkalinities. Mean values are reported for wells which were sampled more than once. Despite the difficulty in obtaining ground water samples which

Table 11.--Water quality in well 130-099-01BBB near Gascoyne, North Dakota

		Concentrations in milligrams per liter or milliequivalents per liter as noted								
		Titration alkalinity meq/L	SO4 mg/L	Cl mg/L	SiO2 mg/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	Percent induced recharge
Collected	pH									
5-25-74	8.3	11.53	570	110	9.1	13	6.4	580	4.4	
6-05-74	8.0	11.29	530	81	9.4	13	7.2	530	5.1	
11-20-74	8.3	11.34	470	40	8.0	16	11	470	5.9	
11-21-74	8.4	10.10	1600	45	10	88	55	820	11	19
4-30-75	8.7	9.82	1100	49	6.9	30	18	710	6.5	
11-05-75	8.6	10.12	1200	39	6.1	21	12	750	6.4	
4-12-76	8.6	10.17	1100	26	6.7	16	9.8	720	6.2	
8-27-78,1000 hrs.	8.6	10.23	980	14	6.4	11	6.5	640	6.3	
8-27-78,1100 hrs.		7.51	3500	14	11	59	42	1700	18	50
Calculated composition of induced recharge		4.80	6000	17	17				31	

Table 12A. Chemical compositions of ground water from the vicinity of Gascoyne, North Dakota

| | | | | Concentrations of dissolved constituents in milligrams per liter (mg/L) or milliequivalents per liter (meq/L) as noted | | | | | | | | | |
Location	Depth below land surface (m)	Color1/	pH	Titration alkalinity meq/L	Sulfate mg/L	Chloride mg/L	Fluoride mg/L	Silica mg/L	Calcium mg/L	Magnesium mg/L	Strontium mg/L	Sodium mg/L	Potassium mg/L
1. Ground waters from the upper 4m of the water table.													
130-099-													
03ADC	7.6	17	7.3	10.2	8800	39	.6	17	440	510	2/—	2800	30
11ADD3	9.4	<10	7.7	9.44	3000	26	1.1	12	200	160	1.4	1020	19
131-099-													
13BAB2	37	—	7.5	12.6	380	4.2	.6	14	99	71	—	210	18
21CCB4	18	<10	7.3	6.29	1500	4.5	.6	14	350	190	2.0	96	15
21CCB5	17	<10	7.2	7.47	1300	6.0	.6	13	270	190	2.9	109	20
27DAA2	12	—	8.1	17.0	830	16	.1	—	95	96	—	560	22
33DCD4	19	75	7.0	14.4	1300	4.9	.8	14	74	50	2.5	790	14
34BAC	6.1	—	7.1	8.13	1400	5.0	1.1	13	250	160	7.3	230	8.0
35BDB2	12	18	6.8	11.6	950	6.9	.3	28	150	88	—	400	17
35BDB3	8.8	<10	7.0	5.1	940	9.0	.6	6.2	170	120	2.0	110	6.8
36BCC3	16	40	7.1	21.0	3900	13	3.2	14	320	370	6.3	1350	34
2. Wells screened in the Harmon lignite.													
131-099-													
12BBB1	52	<10	8.4	7.54	790	10	1.1	8.6	39	16	—	470	10
13BAB1	56	90	9.5	5.09	490	6.1	.9	8.1	15	5.1	—	340	9.8
17ADD1	45	>1500	8.6	13.3	420	14	3.6	5.9	1.3	36	—	430	8.3
17BBB1	50	200	8.8	11.2	290	11	2.9	13	14	6.7	—	360	5.9
21CCB1	24	<10	7.7	6.47	380	4.6	.5	12	131	68	1.7	51	9.2
22DCD	23	<10	7.3	8.51	2000	34	.9	8.3	260	190	3.5	480	15
23CCC2	30	100	8.1	8.98	680	5.6	2.6	7.0	8.6	7.2	.3	530	4.8
26ADA	37	<10	8.5	8.10	970	4.0	1.7	11	14	8.2	.5	630	6.6
26DDD2	23	150	8.6	8.69	310	6.1	2.3	8.0	7.7	1.9	.1	320	3.2
29ADD3	24	—	7.6	9.31	460	7.6	.4	14	42	30	—	310	14
29ADD4	25	<10	7.6	9.75	430	4.7	.6	9.5	24	17	1.0	360	13
3. Wells screened in the confined basal sand.													
131-099-													
17BBB2	68	450	8.6	17.0	83	9.0	6.5	6.7	9.2	3.6	.1	420	5.8
19CCC	24	20	7.6	9.58	1400	10	.6	9.4	130	80	4.9	560	25
21CCC1	56	<10	8.5	12.3	300	20	2.7	9.9	12	3.4	—	410	5.3
22CCB	51	>1500	8.8	16.3	400	38	4.4	11	32	25	.8	490	4.8
23CCC1	52	>1500	8.3	12.6	380	9.9	4.3	7.5	13	5.7	.1	440	5.1
25BBB2	61	>1500	8.5	11.6	140	24	4.2	9.3	4.1	1.3	—	320	2.1
27DDD1	34	>1500	8.6	12.6	190	42	3.6	7.3	9.9	3.1	.2	370	2.4
28DDD	40	—		13.2	520	36	2.4	4.7	9.2	4.3	—	540	5.4
29ADD1	36	1400	8.6	11.7	470	30	1.8	7.0	5.8	3.1	.2	510	4.0
29BBB	41	500	8.8	12.1	280	18	1.2	8.7	12	2.9	—	390	2.9
35BDB1	24	>1500	8.9	11.5	160	18	3.0	14	9.3	2.0	.1	320	3.2
36BBB1	47	>1500	8.8	11.5	170	43	4.9	8.0	6.3	1.6	—	350	2.8

Table 12 A. (cont.)

Concentrations of dissolved constituents in milligrams per liter (mg/L) or milliequivalents per liter (meq/L) as noted

Location	Depth below land surface (m)	Color[1]	pH	Titration alkalinity meq/L	Sulfate mg/L	Chloride mg/L	Fluoride mg/L	Silica mg/L	Calcium mg/L	Magnesium mg/L	Strontium mg/L	Sodium mg/L	Potassium mg/L
4. Wells screened in the unconfined basal sandstone.													
130-099-													
01BBB	18	80	8.5	10.2	1200	46	1.5	8.2	30	19	.9	770	7.8
02CCC2	17	<10	8.6	11.9	900	17	2.8	9.5	11	6.1	.5	690	5.4
03ADD	20	<10	8.9	6.30	2900	16	1.4	8.3	45	48	2.0	1380	18
03BAA	20	70	9.3	7.78	3700	20	1.2	12	50	100	1.8	1690	18
04ADD2	15	<10	7.2	5.38	4800	16	.8	6.7	240	350	3.7	1460	18
04BAA	15	--	7.2	7.93	2200	6.9	.8	13	120	94	4.3	870	17
11ADD1	24	10	9.3	17.9	1000	11	1.2	28	32	5.4	--	880	11
131-099-													
31BAA	12	30	8.1	11.6	1000	4.6	.8	9.0	22	16	.7	690	6.2
32ABB	12	700	9.1	13.4	770	13	2.0	--	31	14	--	600	9.0
32DBC	9.1	350	8.1	11.3	760	7.2	1.2	8.2	52	18	.7	540	8.4
33CCC	18	20	7.7	10.3	1600	6.5	.3	11	130	100	4.2	660	16
33DAA	32	<10	9.3	7.71	2100	13	1.0	30	17	9.6	--	1100	8.9
33DAD2	25	<10	7.8	12.0	6800	12	1.5	11	200	200	9.9	2800	20
34ACC1	35	--	8.7	11.2	940	9.4	2.1	10	18	6.6	.3	680	4.7
34ACC2	12	--	7.6	10.0	1700	7.0	.7	12	87	63	--	800	12
34BAB	11	--	7.6	8.65	820	7.2	1.0	13	64	49	--	450	9.2
34BCA	30	--	8.3	9.30	3600	8.5	.7	8.5	52	43	2.4	1800	13
34DAD2	12	--	7.3	8.60	730	6.7	.9	13	120	90	--	260	9.6
5. High pH waters from the basal sandstone.													
130-099-													
02ABB	23	1250	11.4	13.2	120	23	2.9	18	12	.3	.1	350	4.2
03AAB1	29	20	11.9	11.4	140	9.3	3.3	41	6.0	.3	.1	320	3.4
03ABB	27	10	9.9	2.68	2800	16	1.2	28	135	2.0	--	1300	12
131-099-													
33AAA1	46	125	11.5	7.54	260	9.3	1.6	66	3.8	1.3	.05	290	3.5
33AAA2	27	500	11.0	6.25	1100	7.0	2.1	24	27	2.2	.3	650	7.6
34DAD1	30	80	10.1	5.87	320	9.7	2.1	50	1.7	.4	--	290	1.7
Average values													
Unsaturated zone waters 3/			7.2	8.5	8500	63	1.1	14	310	670	1.9	2500	26
Waters from top 4m of water table			7.3	11.2	2200	12	.9	15	210	180	3.5	700	18
Lignite aquifer waters			8.2	8.8	660	9.8	1.6	9.6	51	35	1.2	390	9.1
Confined basal sand waters			8.5	12.7	370	24	3.3	8.6	21	11	.9	430	5.8
Unconfined basal sand waters			8.3	10.1	2100	13	1.2	12	73	70	2.4	1000	11
High pH waters			10.7	7.8	790	15	2.6	33	29	.6	.1	490	4.8
Average values, wells north of the mine													
Water from top 4m of water table			7.3	8.79	1060	4.9	.6	14	240	150	2.4	139	18
Lignite aquifer waters			8.3	8.73	720	12	1.8	9.0	67	47	1.8	380	9.0
Confined basal sand waters			8.4	13.6	510	17	3.7	8.9	39	24	1.5	460	9.2

1/ Hazen platinum-cobalt scale.
2/ --No data.
3/ From data of Table 10.

are unequivocally representative of undisturbed formation water at screen depth, the existence of some well-defined compositional patterns is evident in the data, and some generalizations about differences in chemistry between the individual groups appear to be justified. Distinctive chemical features that can be associated with one or more of these groups are described below.

Deep color is a characteristic property of most of the water from the confined basal sandstone. After filtration through 0.45μm membranes, the most highly colored waters are black and opaque when viewed through a 5 cm path length in daylight. The source of color is probably organic matter leached from the lignite by recharge water. Chemical characterization of the aqueous phase organic matter was not attempted, although the nature of organic substances removed from the lignite is undoubtedly important to the geochemistry of the ground water system.

A distinct odor of H_2S was present over fresh samples from most of the lignite aquifer wells, several wells in the unconfined basal sand, and two wells in the confined sandstone beneath the lignite. No H_2S odor was detected in samples from wells in the top 4 m of the water table or in the high-pH samples.

Near-neutral pH values are characteristic of waters from the upper few meters of the water table in both the lignite and the basal sandstone aquifer units. pH in most of the deeper ground waters ranges from about 8 to 9, a range which is typical of many aquifers containing both carbonates and silicates. The extremely high-pH waters are from wells in the basal sandstone near the lignite outcrop. Hydroxide alkalinity and high dissolved silica levels indicate that silicate hydrolysis reactions contribute significantly to the observed chemical compositions of these strongly alkaline waters.

Titration alkalinities of the confined sandstone waters are generally greater than, and sulfate concentrations less than, corresponding values for wells screened in the lignite. A very wide range of sulfate concentrations is observed in wells screened near the top of the water table and those in the unconfined basal sandstone. High-sulfate waters (> 2000 mg/L $SO_4^=$) from wells screened more than 10 m below water table are all geographically near, and hydrologically downgradient from, the area where a 9 m thick tongue of the Harmon lignite persists in the unsaturated zone. With two exceptions, wells screened in the lignite and in the confined sandstone yield water containing less than 1000 mg/L sulfate.

Another feature of the dissolved sulfate distribution in Gascoyne area ground waters can be seen in the plot of sulfate concentration as a function of depth below the mean water table (fig. 15). The broken lines connect data points representing waters at different depths in the same quarter-quarter-quarter section. Generally negative slopes of the lines suggest that dissolved sulfate concentrations usually decrease with increasing depth below the water surface at a given geographic location.
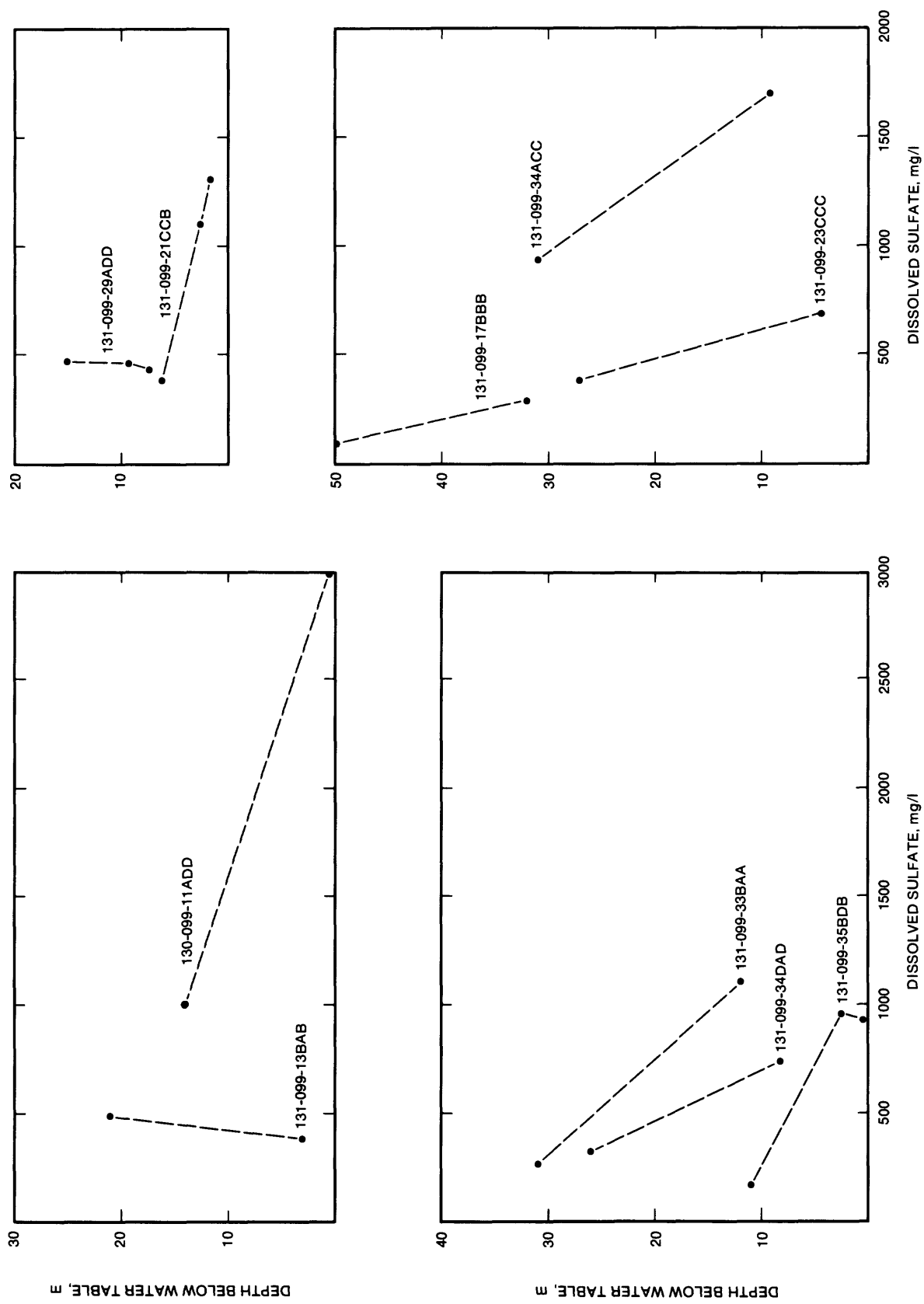
Figure 15. Variations in dissolved sulfate with depth below water table

Average chemical compositions of the various groups of ground waters, including unsaturated-zone waters, also are listed in table 12A. Additionally, averages were calculated for the data from wells north of the mine property; data for these subgroups (table 12A) represent conditions in the upper water table, the lignite and the confined basal sand of a relatively undisturbed ground-water system in an area of intact, saturated lignite and southward ground-water flow.

Averages in table 12A indicate that chloride is highest in the perched waters, presumably as a result of evaporative concentration. Dissolved fluoride, on the other hand, is highest in the confined basal sand, and comparison of the data for the lignite and the basal sandstone wells suggests enrichment of dissolved chloride as well as fluoride in the confined sandstone. Higher halide concentrations in the confined sandstone imply the presence of a source of these ions in or below the Harmon lignite.

Highest average alkaline-earth concentrations are found in samples of the near-neutral perched waters and upper water table waters. In these shallow zones, levels of dissolved calcium and magnesium exceed 100 mg/L. Alkaline earths are evidently removed from water percolating through the lignite aquifer, and are further depleted in water reaching the confined basal sand. Lowest average magnesium and strontium concentrations are found in the high-pH waters.

Average composition data for wells north of the mine (table 12A) indicate regular changes in levels of most of the common ionic constituents of ground water during its flow from the top of the water table to the confined sandstone. Monotonic increases are observed in chloride, fluoride, and sodium, and decreases are noted for concentrations of sulfate, calcium, magnesium, and strontium.

Concentrations of minor and trace elements were determined in a number of the Gascoyne area ground waters. Results of analyses of dissolved iron, manganese, phosphorus, boron, and organic carbon are listed in table 12B. Mean values are reported for wells which were sampled more than once during this study. Levels of dissolved iron in the confined basal sandstone are generally higher than iron concentrations in the unconfined aquifers. Median concentration of dissolved phosphorus is 0.25 mg/L for all of the available data; concentrations in the confined sandstone generally exceed this median value. Median value of dissolved boron is 0.8 mg/L, higher than the value of 0.46 mg/L boron found by Croft (1978) over a larger area of the Tongue River - Upper Ludlow aquifer in southwestern North Dakota. The sparse available data indicate levels of a few tens of mg/L organic carbon in the basal sandstone, and about 5 mg/L in the lignite aquifer.

Dissolved gases in ground waters

Dissolved-gas concentrations were determined in waters from 20 wells in the Gascoyne area. Samples were collected and analyzed by the method described in Hobba and others (1977); results of the analyses are presented in table 13. Mean values are reported for wells sampled more than once during the study period.

Table 12B. **Concentrations of dissolved minor constituents in ground water from the vicinity of Gascoyne, North Dakota**

Location	Concentrations in milligrams per liter (mg/L)				
	Iron	Manganese	Phosphorus	Boron	Organic carbon
Wells screened in the lignite aquifer					
131-099-12BBB1	[1] .02	.00	.25	—	—
131-099-13BAB1	—	—	.09	.39	—
131-099-17ADD1	—	—	—	.0	—
131-099-21CCB1	—	—	—	.66	—
131-099-22DCD	.04	.54	—	.51	4
131-099-23CCC2	.19	.02	.19	—	—
131-099-26ADA	—	—	—	.77	—
131-099-26DDD2	—	—	—	.94	5
Wells screened in the confined basal sand					
131-099-17BBB2	—	—	.55	1.3	—
131-099-19CCC	.10	.05	1.9	—	—
131-099-21CCC1	.85	.05	2.3	—	—
131-099-22CCB	.48	.14	.24	.80	28
131-099-23CCC1	.32	.10	.35	—	—
131-099-25BBB2	.7	.05	.89	—	—
131-099-27DDD1	.56	.11	.65	2.4	—
131-099-28DDD	1.6	.06	.45	—	—
131-099-29ADD1	.82	.10	.7	1.4	—
131-099-29BBB	—	—	—	—	18
131-099-35BDB1	.42	.04	.81	—	—
131-099-36BBB1	.36	.44	.34	.54	46
Wells screened in the unconfined basal sand					
130-099-01BBB	.12	.21	.06	.97	21
130-099-02CCC2	.02	.09	.20	1.1	—
130-099-03ADD	—	—	.08	.97	—
130-099-03BAA	.04	.01	.13	—	—
130-099-04ADD2	—	2.5	—	—	—
130-099-04BAA	.41	.67	.00	—	—
130-099-11ADD1	.03	.02	4.9	—	—
131-099-31BAA	—	—	.11	—	—
131-099-32ABB	.17	.04	1.1	—	—
131-099-32DBC	.06	.21	.28	.73	—
131-099-33CCC	.94	.39	.34	5.6	25
131-099-33DAA	.04	.01	.15	—	—
131-099-33DAD2	.08	.21	.27	4.0	—
131-099-34ACC1	.07	.13	.19	1.0	12
131-099-34BCA	.07	.27	—	1.9	—
High pH waters from the basal sand					
130-099-02ABB	—	—	.17	.84	—
130-099-03AAB1	.07	.00	.27	.45	—
130-099-03ABB	.96	.04	.23	1.4	—
131-099-33BAA1	—	—	.35	.54	—
131-099-33BAA2	—	—	.10	.75	—
131-099-34DAD1	—	—	.15	.65	—

[1] — No data

-57-

Table 13.--Dissolved gases in ground waters from the vicinity of Gascoyne, North Dakota

Location	Depth below land surface (m)	Pressure, atmospheres at 8°C.			Concentration of dissolved gases (mg/L)				
		N_2	Ar	CO_2	N_2	Ar	CO_2	O_2	CH_4
Wells screened in the upper 4m of the water table									
131-099-21CCB5	15.9	.97	.011	.022	24	.82	54	.05	[1] Tr.,<.01
131-099-21CCB4	17.4	1.04	.011	.023	26	.84	55	.6	[2]
131-099-33DCD4	20	.94	.012	.088	23	.88	218	.06	
131-099-36BCC3	16.5	1.08	.009	.050	[3] 27	.63	123	.06	Tr.,<.01
Wells screened in the Harmon lignite									
131-099-21CCB1	24	1.15	.012	.015	28	.88	38 Tr.,<.05		Tr.,<.02
131-099-22DCD	23	1.46	.012	.021	36	.92	50	[4]	Tr.,<.01
131-099-23CCC2	30	1.08	.012	.0024	27	.92	5.9	<.02	.02
131-099-26ADA	37	.96	.012	.0008	24	.93	1.8	<.02	.01
Wells screened in the confined basal sandstone									
131-099-17BBB2	68	1.04	.012	.0040	26	.85	9.7	<.01	.44
131-099-23CCC1	52	1.37	.013	.0013	34	1.0	3.3	<.02	.06
131-099-27DDD1	34	1.18	.013	.0009	30	1.0	2.3	<.02	.02
131-099-29ADD1	36	.95	.012	.0008	24	.91	2.2	<.02	.01
Wells screened in the unconfined basal sandstone									
130-099-03ADD	19.5	1.39	.016	.0009	35	1.2	2.2	.8	.02
130-099-04ADD2	15.2	1.02	.012	.029	26	.86	73	.06	
131-099-32DBC	9.1	1.41	1.41	.0034	36	.58	8.4	<.02	.01
131-099-33DAD2	25	.98	.98	.0047	25	.90	12	<.02	.01
High pH waters in the basal sandstone									
130-099-02ABB	23	1.40	.014	.0001	35	1.1	.3	.10	.02
130-099-03AAB1	29	1.15	.013		29	.99		.11	.01
131-099-33BAA1	46	1.67	.010		42	.77		.11	.01
131-099-33BAA2	27	1.24	.012	.0001	31	.92	.02	<.02	.02

[1] Tr. - Trace present.
[2] No entry indicates Not Detected.
[3] Nitrous oxide occasionally present, in amounts up to 0.7 mg/L.
[4] Measurable dissolved oxygen, in the amount of 2.9 mg/L, in 1 of 2 samples.

Carbon dioxide concentrations exceed 50 mg/L in each of the four wells screened near the top of the water table. Highest concentrations, corresponding to a carbon dioxide partial pressure P_{CO_2} of nearly 0.1 atmospheres (more than 200 mg/L at 8°C) are found in well 131-099-33DCD4, screened in the sand below unsaturated-zone Harmon lignite. High P_{CO_2} in water from this well and the shallow section 36 well are consistent with high unsaturated-zone CO_2 concentrations found in the deep gas probe samples at these locations. P_{CO_2} in the section 21 wells is approximately twice the value calculated for the nearby 8.5 m gas probe. Carbon dioxide pressures in wells deeper than 4 m below the water table are generally less than .01 atmospheres at 8°C. Less than atmospheric values ($\approx$ .0003 atm.) of P_{CO_2} are found in the high-pH waters.

The dissolved gas data indicate that little or no dissolved oxygen is present in ground water in the Gascoyne area. Small amounts of methane were found in water from 17 of the 20 wells sampled. Occasional presence of nitrous oxide in the shallow section 36 well water indicates the occurrence of denitrification near this site.

Tritium and carbonate isotopes in surface and ground water

Samples of Gascoyne area waters were collected for analyses of tritium and of dissolved carbonate isotopes. Results of the analyses are listed in table 14.

Tritiated water in atmospheric precipitation over the northern hemisphere rose sharply as a result of nuclear explosives tests in the 1950's and early 1960's, reaching peak levels of about 5000 tritium units (1 tritium unit [T.U.] = 1 atom ^3H per 10^{18} atoms ^1H) in 1963 in southwestern North Dakota (T.A. Wyerman, U.S. Geological Survey, personal communication, 1982). Radioactive decay and washout are gradually removing this short-lived ($\approx$ 12 year half-life) species from the atmosphere. Since 1963, tritium levels in precipitation over the study area have declined irregularly to less than 100 T.U. in 1976, and to a 1980 level of about 50 T.U. Pre-1953 water, on the other hand, contains less than 1 or 2 mol.^3H per 10^{18} mol.^1H. Thus, as little as 10 percent of "modern" (post-1953) recharge should elevate the tritium content of a Gascoyne area ground water to at least 3 or 4 T.U. A mixture of entirely modern recharge, composited in proportions corresponding to relative annual amounts of precipitation from 1953 to 1978, would produce a water with a tritium level of about 350 T.U. in 1978. Tritium in a modern water collected in 1981, made up of a comparable admixture of precipitation falling between 1953 and 1981, should be about 270 T.U. (data from T.A. Wyerman, U.S. Geological Survey, personal communication, 1982).

Compositions of the low-flow September 1981 stream samples probably are dominated by the ground-water component. The high-flow samples, on the other hand, consist mostly of fresh rain and snow melt; observed tritium levels of several tens of tritium units in these samples indicate that substantial amounts of tritiated water continued to fall on southwestern North Dakota in 1982.

Location	Depth below land surface m	Collected Mo.	Yr.	Tritium T.U. $\pm$ 1σ[1]	Isotopes in dissolved carbonate species $\delta^{13}C$ [2]	$\delta^{18}O$ [3]
Surface waters						
130-099-03ADD [4]		9	81	15.8 $\pm$ .9	-- [5]	--
		5	82	35.6 $\pm$ 1.3	--	--
131-099-22CCC [6]		9	81	14.3 $\pm$ .9	--	--
		6	82	50.4 $\pm$ 1.8	--	--
Unsaturated zone waters						
131-099-36BCC	5.2	6	77	--	-8.73	+18.94
Wells in the upper 4m of the water table						
130-099-11ADD3	9.4	6	77	--	-15.47	+14.94
131-099-21CCB4	18	8	80	.7 $\pm$ .5	--	--
		3	81	.2 $\pm$ .1	--	--
		6	81	.1 $\pm$ .1	--	--
		10	81	.2 $\pm$ .1	--	--
131-099-21CCB5	17	8	80	2.8 $\pm$ .4	--	--
		6	81	1.6 $\pm$ .1	--	--
		10	81	2.7 $\pm$ .2	--	--
131-099-33DCD4	19	8	80	0 $\pm$ .4	--	--
		3	81	.2 $\pm$ .1	--	--
		6	81	.4 $\pm$ .1	--	--
		10	81	.3 $\pm$ .1	--	--
131-099-35BDB3	8.8	6	77		-16.95	+11.32
131-099-36BCC3	16	8	80	16.6 $\pm$ .7	--	--
		3	81	25.2 $\pm$ 1.0	--	--
		6	81	29.0 $\pm$ 1.5	--	--
		10	81	21.3 $\pm$ .8	--	--
Wells screened in the lignite						
131-099-21CCB1	24	7	77	--	-8.28	+16.87
		8	80	139 $\pm$ 8	--	--
		3	81	131 $\pm$ 5	--	--
		6	81	178 $\pm$ 5	--	--
		10	81	129 $\pm$ 6	--	--
131-099-22DCD	23	8	78	174 $\pm$ 6	--	--
		5	79	162 $\pm$ 6	--	--
		8	80	156 $\pm$ 5	--	--
		9	81	147 $\pm$ 6	--	--
131-099-23CC2	30	5	79	.2 $\pm$ .1	--	--
		8	80	.7 $\pm$ .1	--	--

Table 14.--(Continued)

Location	Depth below land surface m	Collected Mo.	Collected Yr.	Tritium T.U. $\pm$ 1σ[1]	Isotopes in dissolved carbonate species $\delta^{13}C$ [2]	Isotopes in dissolved carbonate species $\delta^{18}O$ [3]
Wells screened in the lignite (Continued)						
131-099-26ADA	37	9	76	--	-10.20	+17.55
		5	79	.6 $\pm$ .1	--	--
		10	81	1.4 $\pm$ .1	--	--
131-099-26DDD2	23	9	76	--	-9.86	+17.47
		7	77	--	-9.82	+17.77
131-099-29ADD4	25	10	81	.1 $\pm$ .1	--	--
Wells screened in the confined basal sand						
131-099-17BBB2	68	8	80	.3 $\pm$ .1	--	--
131-099-23CCC1	52	8	80	.1 $\pm$ .1	--	--
131-099-29ADD1	36	9	76		-10.54	+17.62
		10	81	.2 $\pm$ .1	--	--
Wells screened in the unconfined basal sand						
130-099-01BBB	18	8	78 [7]	8.5 $\pm$ .8	--	--
		8	78 [8]	6.8 $\pm$ .8	--	--
130-099-02CCC2	17	7	77	--	-8.14	+17.83
		10	81	.2 $\pm$ .1	--	--
130-099-03ADD	20	8	78	.9 $\pm$ .8	--	--
		10	81	.4 $\pm$ .1	--	--
130-099-03BAA	20	5	79	1.0 $\pm$ .1	--	--
130-099-04ADD2	15	5	79	.2 $\pm$ .1	--	--
		10	81	1.5 $\pm$ .1	--	--
130-099-04BAA	15	7	77	--	-15.14	+18.50
		8	78	.7 $\pm$ .8	--	--
131-099-31BAA	12	10	81	.3 $\pm$ .1	--	--
131-099-32DBC	9.1	9	76	--	- 8.79	+17.89
131-099-33DAD2	25	7	77	--	-11.70	+19.85
		8	78	0 $\pm$ .8	--	--
High pH waters in the basal sand						
130-099-02ABB	23	10	81	.3 $\pm$ .1	--	--
130-099-03AAB1	29	10	81	.3 $\pm$ .1	--	--
131-099-33BAA2	27	10	81	.7 $\pm$ .1	--	--

[1] One standard deviation.
[2] Relative to the PDB standard.
[3] Relative to SMOW.
[4] Buffalo Creek tributary below mine; USGS Water Resources Div. station no. 06355310.
[4] -- No data.
[5] Buffalo Creek tributary above mine; USGS Water Resources Div. station no. 06355308.
[7] Sampled at 1000 hrs.
[8] Sampled at 1100 hrs.

At 18 of 23 ground water sites sampled, including two wells in the upper 4 m of the water table, tritium concentrations are less than 2 T.U.; such low levels of tritium imply an extremely small component of post-1953 precipitation in the ground water reservoirs at these locations. Significant components of modern recharge are indicated by the tritium contents of water from well 130-099-01BBB in the unconfined basal sand and well 131-099-36 BCC3 in the upper 4 m of the water table.

Major amounts of post-bomb water (approximately 50 percent based on a precipitation-weighted composite of post-1953 rain and snow) are present in the lignite wells at sections 21 and 22. Observed annual decreases in tritium level of the section 22 water (table 14) correspond well with the expected decay losses of a 50 percent modern water. The virtual absence of tritium in the shallower wells at section 21CCB, in contrast to very high tritium concentrations in the lignite well in the same quarter-quarter-quarter section, indicates that vertical seepage does not contribute substantially to recharge of the lignite at this location. Both high-tritium wells are less than 1 km north of active mine pits; dewatering operations at the mine probably accelerated ground water flow at these well sites and may have induced the flow of modern recharge through particularly permeable strata upgradient from the wells.

The tritium data provide valuable information on the time scale of subsurface water movement in the Gascoyne area. Most of the analyzed ^{3}H concentrations are low, indicating very small post-1953 contributions to the ground water reservoirs. Low tritium levels in three wells screened near the water table surface provide good evidence that annual recharge by vertical downward percolation of local precipitation is probably very limited over most of the study area. On the other hand, the exceptionally high ^{3}H contents of wells 131-099-21CCB1 and 131-099-22DCD demonstrate the penetration of modern water into the lignite at these locations. Houghton (1982a) has observed sand channels at the top of the Harmon lignite bed, and has suggested that such channels are the principal conduits for ground water flow in the Gascoyne area. Channeled, largely lateral subsurface flow could explain the anomaly of modern water in the lignite at 131-099-21CCB beneath shallow wells containing insignificant amounts of post-bomb water.

Carbon-13 determinations on 11 ground waters in the Gascoyne area yielded $\delta^{13}C$ values ranging from -8.1 to -17. The range indicates mixtures of variable proportions of light carbon from the oxidation of organic matter with heavier carbon from dolomite and calcite dissolution in the dissolved carbonate species.

Mineral-water equilibrium relationships

The computer program WATEQF (Plummer and others, 1976) was used to calculate equilibrium relationships among various minerals and the waters from the Gascoyne area. The program calculates Eh (from electrode potential measurements, dissolved oxygen, or sulfate-sulfide data), concentrations of possible redox pairs, complex ion pairing, carbonate speciation, and ion activities, and produces a refined, internally consistent description of the dissolved species distribution from the input information. Appropriate activity proucts (IAP)

are then computed and compared with equilibrium constants (KT) for the possible mineral sources or sinks at a specific temperature, and the results of these computations are included in the WATEQF output. A temperature of 8°C was assumed for all of the Gascoyne waters. Also, in wells for which dissolved gas data were available (table 13), the pH was adjusted as suggested in Pearson and others (1978) to bring computed P_{CO_2} into agreement with the value determined from dissolved gas analyses.

Computer output data for P_{CO_2}, total carbonate species, and IAP/KT ratios for several minerals are listed in table 15. A positive value of the log (IAP/KT) term indicates supersaturation of the aqueous phase with the mineral, and the mineral should eventually precipitate; a negative log (IAP/KT) value implies undersaturation, in which case dissolution of the solid mineral is thermodynamically favored.

High CO_2 partial pressures (> .02 atmospheres) are present in several of the perched waters and ground waters from the upper water table (table 15). Much lower CO_2 pressures are characteristic of the lignite and basal sand wells. In the high-pH waters, pressures of CO_2 are well below the atmospheric value of ~ .0003 atmospheres. Overall, the range of total CO_2 molalities for the sampled waters is also wide – from .0001 in the acidic perched water at 130-099-12BCC to .048 in the mirabilite-saturated brine from 130-099-02ADA. Within the lignite and confined basal sand groups, however, concentrations of total carbonate species are relatively uniform. Average total CO_2 molality in the lignite is .0089 mol per kg water; the mean value for the confined sandstone wells is .0125 mol per kg.

Substantial supersaturation of most of the Gascoyne waters with calcite and dolomite is indicated in the computer output data of table 15. Exceptions include the high P_{CO_2} (low pH) shallow waters from reclaimed spoils (section 35), from beneath unsaturated-zone lignite (section 33), and from perched water and shallow well waters in the basal sand in township 130. The ponded brines from township 130 are extremely supersaturated with magnesite; elsewhere in the Gascoyne area, log (IAP/KT) values for magnesite usually are less than the calcite values; 18 of the well waters are at or near equilibrium with magnesite. The available data suggest that Gascoyne ground waters are undersaturated with strontianite.

Five of the surface and unsaturated-zone waters are supersaturated with gypsum. Below the water table, only one of 55 ground waters contained dissolved calcium and sulfate ions with an activity product in excess of the gypsum KT value, and only one of 41 subsurface waters was supersaturated with the strontium sulfate, celestite. The lignite and confined sandstone ground waters are generally highly undersaturated with gypsum; activity products for half of the confined sand samples are more than two orders of magnitude less than the equilibrium value. A similar trend of decreasing IAP/KT ratios with depth from shallow wells to confined sandstone wells is evident in the WATEQF data for celestite.

Table 15. Mineral-water equilibrium relationships in waters from the vicinity of Gascoyne, North Dakota

Location	Depth below land surface (m)	pH	Pco2[1] (atmospheres)	Calculated[2] total carbonate species (molality)	Log (IAP/KT) at 8°C[2] Calcite	Magnesite	Strontianite	Dolomite	Gypsum	Celestite	Chalcedony	Quartz
Ponded surface waters												
130-099-01ACC		7.8	.018	.045	+1.4	+2.1	+.6	+3.8	+.7	+.7	+.2	+.7
130-099-01BCB		7.9	.0065	.013	+1.0	+1.1	+.1	+2.4	-.1	-.1	-.1	+.4
130-099-02ADA		8.0	.0048	.048	+1.2	+2.8	+.7	+4.2	+.8	+1.1	+.2	+.8
130-099-34CCB		7.9	.0031	.0058	+.6	+.7	-.3	+1.6	-.5	-.5	<-1	<-1
Unsaturated-zone waters												
130-099-11ADD,	4.9	8.2	.0008	.0035	+.5	+.6	-.3 [3]	+1.3	.0	-.1	+.2	+.7
130-099-12BCC,	4.9	5.3	.019	.0001	-3.7	-3.5	3/—	-7.0	+.3	—	+.2	+.8
131-099-26DDD,	6.1	7.1	.062	.027	-.4	+.5	—	+.4	-.3	—	+.1	+.7
131-099-28CCC,	7.6	7.9	.0019	.0044	+.6	+.7	-1.4	+1.6	+.2	-1.0	-.2	+.3
131-099-33DCD,	10	6.8	.064	.014	+.1	-.3	—	+.1	+.2	—	+.4	+.9
131-099-36BCC,	5.2	7.9	.0039	.0091	+.4	+1.0	-.4	+1.6	-.2	-.2	+.1	+.6
Wells in the upper 4m of the water table												
130-099-03ADC	7.6	7.3	.018	.011	+.3	+.2	—	+.8	+.3	—	+.2	+.8
130-099-11ADD3	9.4	7.7	.0076	.0098	+.5	+.3	-.8	+1.1	-.2	-.8	.0	+.6
131-099-13BAB2	37	7.5	.018	.014	+.5	+.1	—	+.9	-.9	—	+.1	+.6
131-099-21CCB4	18	7.1	.022	.0075	+.1	-.3	-1.3	+.1	-.1	-.8	+.1	+.6
131-099-21CCB5	17	7.2	.022	.0087	+.1	-.1	-1.0	+.3	-.3	-.7	+.1	+.6
131-099-33DCD4	19	6.9	.091	.021	-.3	-.7	-1.0	-.7	-.6	-.6	+.1	+.6
131-099-34BAC	6.1	7.1	.027	.0097	+.1	-.2	-.6	+.2	-.2	-.2	+.1	+.6
131-099-35DB2	12	6.8	.080	.016	-.2	-.6	—	-.5	-.5	—	+.4	+1.0
131-099-35DB3	8.8	7.0	.022	.0064	-.3	-.6	-1.5	-.6	-.4	-.9	-.3	+.3
131-099-36BCC3	16	7.2	.053	.024	+.5	+.4	-.4	+1.2	.0	-.2	+.1	+.7
Wells in the lignite												
131-099-12BBB1	52	8.4	.0013	.0075	+.6	+.1	—	+1.0	-1.1	—	-.1	+.4
131-099-13BAB1	56	9.5	.0001	.0044	+1.1	+.4	—	+1.8	-1.6	—	-.2	+.3
131-099-17ADD1	45	8.6	.0014	.013	-.4	+.9	—	+.8	-2.8	—	-.3	+.3
131-099-17BBB1	50	8.8	.0008	.011	+.8	+.3	—	+1.4	-1.8	—	+.1	+.6
131-099-21CCB1	24	7.3	.016	.0074	+.1	-.4	-1.1	.0	-.8	-1.2	.0	+.6
131-099-22DCD	23	7.2	.020	.0096	+.2	-.1	-.9	+.4	-.1	-.5	-.1	+.4
131-099-23CCC2	30	8.2	.0025	.0090	-.1	-.4	-.8	-.2	-1.8	-1.8	-.2	+.4
131-099-26ADA	37	8.6	.0008	.0079	+.4	.0	-.3	+.7	-1.5	-1.5	.0	+.5
131-099-26DDD2	23	8.6	.0010	.0086	+.3	-.5	-.8	+.1	-2.0	-2.5	-.2	+.4
131-099-29DD3	24	7.6	.011	.0099	+.1	-.3	—	+.1	-1.2	—	+.1	+.6
131-099-29ADD4	25	7.6	.011	.010	+.1	-.3	—	+.1	-1.2	—	+.1	+.6

Table 15 (continued)

Location	Depth below land surface (m)	pH	Pco2 (atmospheres)	Calculated total carbonate species (molality)	Log (IAP/KT) at 8°C.							
					Calcite	Magnesite	Strontianite	Dolomite	Gypsum	Celestite	Chalcedony	Quartz
Wells in the confined basal sand												
131-099-17RBB2	68	8.2	.0043	.017	+.4	-.2	-1.0	+.4	-2.5	-3.1	-.2	+.3
131-099-19CCC	24	7.6	.010	.010	+.4	.0	-.3	+.7	-.5	-.4	-.1	+.5
131-099-21CCC1	56	8.5	.0017	.012	+.5	-.2	--	+.6	-1.9	--	-.1	+.5
131-099-22CCB	51	8.8	.0011	.016	+1.3	+1.0	+.4	+2.6	-1.4	-1.6	.0	+.5
131-099-23CCC1	52	8.6	.0014	.012	+.6	+.1	-.8	+1.0	-1.8	-2.5	-.2	+.4
131-099-25BBB2	61	8.5	.0017	.012	+.7	-.6	--	-.2	-2.6	--	-.1	+.5
131-099-27DDD1	34	8.8	.0010	.012	+.7	.0	-.2	+1.0	-2.1	-2.4	-.2	+.3
131-099-29ADD1	36	8.8	.0009	.011	+.4	-.1	-.3	+.6	-2.1	-2.0	-.2	+.4
131-099-29BBB	41	8.8	.0008	.012	+.8	.0	-.6	+1.1	-1.9	-2.6	-.1	+.4
131-099-35BDB1	24	8.9	.0006	.011	+.8	-.1	--	+1.0	-2.2	--	+.1	+.6
131-099-36BBB1	47	8.8	.0008	.011	+.5	-.3	--	+.6	-2.4	--	-.2	+.4
Wells in the unconfined basal sand												
130-099-01BBB	18	8.5	.0014	.010	+.7	+.3	-.1	+1.3	-1.1	-1.1	-.1	+.4
130-099-02CCC2	17	8.6	.0013	.012	+.4	.0	-.1	+.7	-1.6	-1.5	-.1	+.5
130-099-03ADD	20	8.4	.0011	.0062	+.3	+.2	-.2	+.9	-.8	-.6	-.1	+.4
130-099--3BAA	20	9.3	.0001	.0067	+1.2	+1.4	+.6	+2.9	-.8	-.6	.0	+.5
130-099-04ADD2	15	6.8	.031	.0071	-.6	-.6	-1.6	-.9	.0	-.3	-.2	+.3
130-099-04BAA	15	7.2	.021	.0091	-.2	-.5	-.8	-.4	-.4	-.4	+.1	+.6
130-099-11ADD1	24	9.3	.0003	.016	+1.6	+.6	--	+2.5	-1.2	--	+.4	+.9
131-099-31RAA	12	8.1	.0040	.012	+.2	-.1	-.5	+.5	-1.3	-1.3	-.1	+.5
131-099-32DBC	9.1	8.1	.0036	.011	+.7	.0	-.4	+1.0	-1.0	-1.4	-.1	+.5
131-099-33CCC	18	7.7	.0086	.011	+.5	+.2	-.2	+1.0	-.4	-.4	.0	+.5
131-099-33DAA	32	9.3	.0001	.0068	+.9	+.5	--	+1.7	-1.3	--	+.4	+.9
131-099-33DAD2	25	8.0	.0050	.012	+.7	+.6	+.3	+1.5	-.1	+.2	.0	+.6
131-099-34ACC1	35	8.7	.0009	.011	+.7	+.1	-.3	+1.1	-1.4	-1.7	.0	+.5
131-099-34ACC2	12	7.6	.011	.011	+.2	-.1	--	+.4	-.6	--	.0	+.6
131-099-34BAB	11	7.6	.0092	.0092	+.1	-.2	--	+.2	-.9	--	+.1	+.6
131-099-34BCA	30	8.3	.0018	.0092	+.5	+.2	.0	+1.0	-.7	-.5	-.1	+.4
131-099-34DAD2	12	7.3	.019	.0097	+.1	-.2	--	+.2	-.6	--	+.1	+.6
High pH wells in the basal sand												
130-099-02ABB	23	11.4	<.00001	.0046	+1.6	-.1	--	+1.8	-2.5	-3.0	-1.0	-.4
130-099-03AAB1	29	11.9	<.00001	.0027	+1.2	-.3	--	+1.2	-2.7	-2.9	-1.2	-.6
130-099-03ABB	27	9.9	<.00001	.0020	+1.6	-.3	--	+1.6	-.3	--	+.2	+.8
130-099-33RAA1	46	11.5	<.00001	.0020	+.9	+.3	--	+1.5	-2.5	-2.9	-.5	+.0
131-099-33BAA2	27	11.0	<.00001	.0025	+1.6	+.4	--	+2.2	-1.3	-1.6	-.5	+.1
131-099-34DAD1	30	10.1	<.00001	.0040	+.5	-.3	--	+.5	-2.8	--	+.4	+1.0

Table 15 (continued)

Location	Depth below land surface (m)	pH	Pco2 (atmospheres)	Calculated total carbonate species (molality)	Log (IAP/KT) at 8°C							
					Calcite	Magnesite	Strontianite	Dolomite	Gypsum	Celestite	Chalcedony	Quartz
Average values, wells north of the mine												
Wells in upper 4m of the water table		7.3	.019	.0098	+.4	.0	-.9	+.6	-.3	-.8	+.1	+.6
Wells in the lignite		8.3	.0019	.0087	+.9	+.5	.0	+1.7	-.9	-1.0	-.1	+.5
Wells in the confined basal sand		8.4	.0024	.014	+.9	+.5	+.2	+1.7	-1.2	-1.2	-.1	+.4

1/ Calculated by WATEQF (Plummer and others, 1976) when not determined analytically.
2/ Calculated by WATEQF (Plummer and others, 1976).
3/ -- No data.

Equilibrium data for chalcedony and quartz indicate that most of the Gascoyne ground waters are at or near equilibrium with chalcedony. The high pH waters from 131-099-33BAA appear to be in equilibrium with quartz. The high dissolved silica values in these wells include significant concentrations of the $H_3SiO_4^-$ anion.

Iron mineral saturation data also were calculated by the WATEQF program for wells north of the mine. Average dissolved iron concentrations for the lignite and confined sandstone wells, and estimated hydrogen sulfide levels of .001 mg/L and .0001 mg/L in the lignite and confined sandstone aquifers, respectively, were used as input data for the computer calculations. Eh values for the lignite and confined sandstone aquifers were computed from the sulfide-sulfate input data. The calculated log (IAP/KT) results are substantially greater than 1 for pyrite, and less than -1 for freshly precipitated ferrous sulfide, indicating stability of FeS_2, and reactivity of solid FeS, in both aquifer units. Comparable data for ferric iron species suggest insolubility of crystalline goethite, but undersaturation with amorphous ferric hydroxide in the lignite and confined sand waters. The computer data also indicate near-equilibrium (log (IAP/KT) = -.2) between lignite water and siderite, and substantial supersaturation (log (IAP/KT) = +.8) of this mineral in the confined sand aquifer.

ASSESSMENT OF GEOCHEMICAL PROCESSES AT GASCOYNE

Generalizations and hypotheses concerning the aqueous geochemistry at Gascoyne are presented below. The proposed reactions are consistent with the available data, and are generally recognized as potentially important to water quality. However, the hypotheses must be regarded as tentative; more detailed chemical, biological, and hydrologic studies will be required in order to develop a comprehensive description of mineral-water interactions in the fine-grained, heterogeneous sediments of the Fort Union Formation.

Unsaturated Zone Reactions

Ground-water recharge in the Gascoyne area is exposed at very shallow depths to carbonate and sulfate minerals. Reactions of these minerals with unsaturated-zone water probably provide much of the alkalinity, sulfate, and alkaline earth cations in the shallow-water-table wells.

Dissolution of an alkaline earth carbonate is ultimately limited by the metal ion-carbonate activity product constant for the particular mineral. In a closed system, pure water will dissolve calcite to produce a highly alkaline aqueous solution containing about 5 mg/L of calcium, with a distribution of carbonate species determined by carbonate-bicarbonate-carbon dioxide equilibrium constants. However, a significant reservoir of gas-phase carbon dioxide in the unsaturated zone Gascoyne sediments can alter the closed-system conditions. CO_2 derived from root respiration and from decay of modern plants and lignite

will dissolve in infiltrating water until partial pressures of CO_2 are equal in the vapor and liquid phases of the unsaturated zone. Dissolution of calcite (and other carbonate minerals) will then proceed in the CO_2-charged water until the constraints of the metal ion-carbonate activity product and the vapor-liquid CO_2 pressure equality are simultaneously satisfied. At a P_{CO_2} of 0.02 atmospheres, for example, saturation of pure water with calcite yields a solution containing 130 mg/L calcium and about 400 mg/L bicarbonate at a pH of approximately 7.3. In waters containing high concentrations of sodium sulfate, ion pairing reduces the free calcium and carbonate ion activities and permits further dissolution of calcite at a particular unsaturated-zone P_{CO_2}.

The processes are summarized in the equations below, in which M represents an alkaline earth metal.

Dissolution of unsaturated-zone CO_2 in recharge water

$$CO_2(g) = CO_2(aq.)$$

At equilibrium, $P_{CO_2}(g) = P_{CO_2}(aq)$
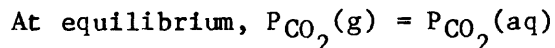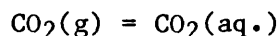
Distribution of the dissolved carbonate species

$$CO_2(aq) + H_2O = H_2CO_3 = H^+ + HCO_3^- = 2H^+ + CO_3^=$$
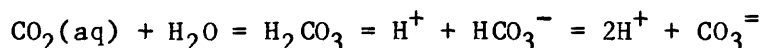
Equilibrium distribution is governed by dissociation constants of carbonic acid and bicarbonate, and a hydration constant for $CO_2(aq)$.

Dissolution of mineral carbonate

$$MCO_3 + CO_2(aq) + H_2O = M^{+2} + 2HCO_3^-$$
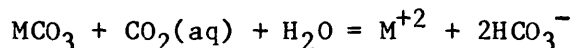
At equilibrium, $(a_M^{+2})(a_{CO_3}^{-2})$ = ion activity product constant for MCO_3.

Ion pairing

$$M^{+2} + SO_4^{-2} = MSO_4(aq)$$

$$Na^+ + CO_3^{-2} = NaCO_3^-(aq)$$
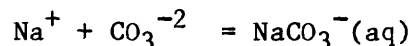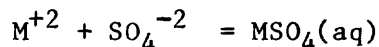
Equilibrium constants for all of the above equations are generally dependent on temperature and ionic strength of the aqueous solution. The carbonate-dissolution reactions are relatively slow.

Evidence for the unsaturated-zone dissolution of alkaline-earth carbonates at Gascoyne is provided by: a) High levels of bicarbonate alkalinity and of alkaline earth cations in five of the six perched ground waters; b) presence

of substantial subsurface gaseous CO_2 at the sites where gas probe data are available; and c) X-ray diffraction analyses that show major amounts of calcite and/or dolomite in the sediments. Considerable supersaturation of three of the perched-water samples may result from evaporative concentration (and slow re-precipitation) in the shallow subsurface. Near equilibrium of the aqueous phase with dolomite, abundance of dolomite and absence of calcite in the sediment column, and a 1:1 mol ratio of calcium to magnesium in the 10 m sample from section 33 suggest that dolomite is dissolving in this high-P_{CO_2} environment.

Small amounts of the ferrous carbonate, siderite, are also present in some shallow horizons of the Gascoyne sediments. Siderite will dissolve in CO_2-charged waters, as do the alkaline earth carbonates, to yield a metal ion-bicarbonate solution. However, dissolved ferrous iron is unstable in an oxygenated environment. O_2 dissolved from the gas phase will oxidize ferrous ion by the reaction

$$O_2 + 4Fe^{+2} + 8HCO_3^- + 10H_2O = 4Fe(OH)_3 + 8H_2CO_3.$$
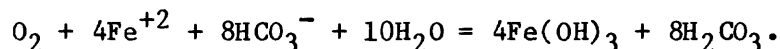
The reaction proceeds spontaneously, and equilibrium lies far to the right, so that ferrous ion will be almost completely removed from oxygenated recharge waters by precipitation as ferric hydroxide. The amorphous precipitate gradually loses water and forms more stable crystalline iron oxyhydroxides. Removal of ferrous iron and generation of carbonic acid by the oxidation reaction will facilitate further dissolution of siderite, and the process will continue to the eventual destruction of this mineral in aerated environments.

Sulfate is the dominant anion in water in the unsaturated zone at Gascoyne waters. Sources of sulfate include the highly soluble sodium- and sodium-magnesium sulfate evaporites as well as surface and subsurface gypsum. Dissolution of evaporites can contribute significantly to recharge water mineralization in topographically low parts of the study area. At higher elevations north of the mine, gypsum is probably the principal source of the dissolved sulfate found in the shallow ground water. Gypsum in the unsaturated-zone leonardite at section 33 (Township 131) also constitutes a massive sulfate source for recharge to the basal sandstone in the southern part of the mine area.

Gypsum dissolves fairly readily in pure water to the ion activity product limit. About 2400 mg/L of pure gypsum (corresponding to approximately 1,350 mg/L SO_4^{-2}) will dissolve in water at 8°C. Some increase in solubility beyond the pure water-gypsum value is provided by sodium-sulfate and calcium-carbonate ion pair formation and some calcite precipitation in the Gascoyne shallow waters. However, ion exchange reactions throughout the unsaturated-zone sediments are probably the principal processes involved in lowering calcium activity to permit continued dissolution of gypsum and steadily increasing dissolved sulfate levels. Removal of calcium by cation exchange is favored on the clays and the lignite in the Gascoyne area. Evaporative concentration may account for the moderate gypsum supersaturation (log [IAP/KT] = + .2 or + .3) in three of the perched waters.

Reactions in the Lignite and Confined Sandstone Aquifer

The perched waters from the Gascoyne area are unequivocally derived from interaction of dilute local recharge with the Fort Union sediments. However, the chemical compositions of the highly mineralized unsaturated zone samples are not representative of water quality in the water-table aquifers. The presence of perched water zones reflects the presence of discontinuous confining beds that impede downward percolation of ground waters; slower movement of the water permits more thorough leaching of soluble salts, more extensive ion-exchange reactions, and evaporative concentration. The volumetric contribution of this perched water to the water-table reservoirs is probably small. Water moving through more permeable subsurface paths is the likely major source of recharge to the water table, and therefore the chemical make-up of the upper 4 m samples rather than the perched waters is the appropriate starting point for examining the changes which occur in the shallow Gascoyne aquifers.

At a few locations in the study area, oxygen is completely consumed in the unsaturated zone. At the section 33DCD gas sampling site, oxygen is removed by reaction with unsaturated lignite. In the section 35BDB unsaturated-zone spoils, oxygen depletion accompanied by a less-than-equivalent increase in CO_2 in the deeper probes suggests the occurrence of an additional reaction, possibly sulfide oxidation, which does not involve carbon. In general, however, high levels of oxygen persist deep into the unsaturated zone and probably to the water table surface over much of the Gascoyne area north of the mine. Gas analyses show the presence of about 19 percent O_2 (nearly equal to the atmospheric value) 8.5 m deep in the unsaturated zone at section 21CCB. In the nearby shallow water-table wells, dissolved oxygen concentrations are low, and in the deeper lignite wells oxygen is virtually absent. Evidently the downward penetration of atmospheric oxygen is effectively halted near the water-table surface. Reductants that may contribute to oxygen removal in the upper water table include siderite, the iron disulfides, methane, hydrogen sulfide, and lignite. The stoichiometry of the reactions is summarized below.

(<u>Siderite</u>): $O_2 + 4\ FeCO_3 + 10H_2O = 4Fe(OH)_3 + 4H_2CO_3$.

(<u>Pyrite, marcasite</u>): $15\ O_2 + 4FeS_2 + 16\ HCO_3^- + 14\ H_2O = 4\ Fe(OH)_3 + 8\ SO_4^{2-} + 16\ H_2CO_3$.

(<u>Methane</u>): $2\ O_2 + CH_4 = H_2O + H_2CO_3$.

(<u>Hydrogen sulfide</u>): $2\ O_2 + H_2S + 2HCO_3^- = SO_4^{2-} + 2H_2CO_3$.

(<u>Lignite</u>): $O_2 + (CH_2O) = H_2CO_3$, in which (CH_2O) represents a reactive lignite component of assumed simple carbohydrate composition.
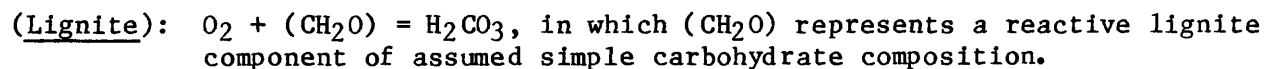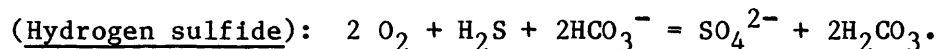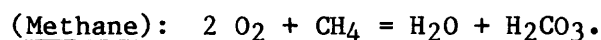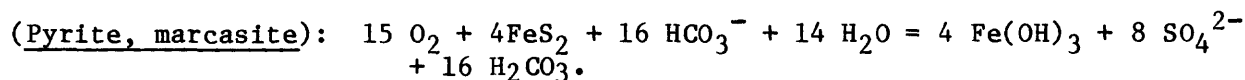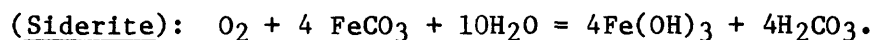
All of the above reactions are thermodynamically feasible—that is, equilibrium oxygen concentrations will be very low even at low concentrations of the reductant. The siderite reaction will occur abiotically; significant rates for the other reactions probably require microbial catalysis. The oxygen-consuming

reactions all generate acidity, indicated above as carbonic acid. Oxidation of siderite, methane, and lignite also increase the concentrations of total dissolved CO_2 species.

The WATEQF output data indicate an average P_{CO_2} of .019 atm. and a pH of 7.3 in the shallowest water table wells north of the mine, and a P_{CO_2} of .0019 atm and pH of 8.3 in the lignite-screened wells below. If the lignite aquifer water was initially saturated with 11 mg/L oxygen at a pH of 8.3, and if oxygen was removed by the siderite reaction near the water table surface, then 1.3 mmol/L H_2CO_3 would be generated, and the resulting deoxygenated water would have a P_{CO_2} of .025 atm. and a pH of 7.2, results which are in fair agreement with the average value data for the upper water table wells. The CO_2 produced at very shallow depths could escape from the ground water system by outgassing into an unsaturated zone with a lower P_{CO_2}.

If the averages of chemical data for wells north of the mine accurately describe the compositions of ground water throughout the lignite aquifer, then observed differences in water chemistry between the upper 4 m waters and those from lignite-screened intervals must result from reactions occurring in the aquifer. Changes from the upper water table to the lignite include significant increases in dissolved chloride, fluoride, and sodium, and marked decreases in concentrations of sulfate, silica, alkaline earth cations, and potassium. The 1 pH unit difference is assumed to reflect the effects of elevated P_{CO_2} levels resulting from oxygen-removal reactions near the water table surface.

Net loss of alkaline earths between the shallowest wells and the lignite is 8.57 millimoles per liter (mmol/L) (from data of table 12A). The observed net increase in sodium (after taking into account the changes in potassium and the halides, and assuming association of alkali cations with halide anions throughout the system) is 9.99 mmol/L. The sodium is probably derived from cation exchange reactions, which remove equivalent quantities of alkaline earths from solution according to reaction (1):

$$Na_2X + M^{2+} = MX + 2Na^+ \quad , \tag{1}$$

where X represents clay minerals or lignite with active exchange sites, and M^{2+} is an alkaline earth cation. The exchange reaction accounts for removal of 5.00 mmol/L of the alkaline earths; removal of an additional 3.57 mmol/L of the alkaline earths must be accomplished by some other precipitation mechanism.

The WATEQF data indicate undersaturation of gypsum and celestite in the shallow ground water, and the magnesium sulfate epsomite is extremely soluble, so that the alkaline earths cannot be removed by precipitation as the sulfates. On the other hand, the shallowest waters have reached saturation with alkaline earth carbonates. Calcite is supersaturated, and should precipitate in the upper water table and in the lignite. However, in the absence of any other reaction,

the simultaneous removal of carbonate with calcium would rapidly lower the ion activity product to the equilibrium value after deposition of only a few tenths of a mmol/L of calcite. Additional reactions must sustain dissolved carbonate levels in order to deposit significant amounts of the alkaline earths as carbonates in the shallow aquifers as indicated below.
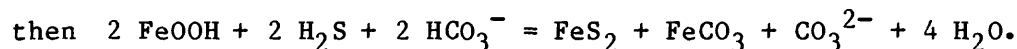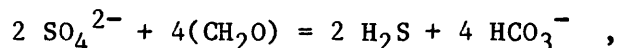
Dissolved sulfate decreases with increasing depth below water table over much of the Gascoyne area. Loss of sulfate by sulfate reduction, which occurs in many anoxic sediments, is attributed to interaction of sulfate with organic matter. The process is catalyzed by bacteria, and the reduced sulfur is ordinarily deposited as the iron disulfides, pyrite and marcasite. At Gascoyne, the Harmon lignite provides an enormous reservoir of organic matter that can serve as the reducing agent for sulfate and ferric iron in the reaction

$$8SO_4^{2-} + 4FeOOH + 15(CH_2O) = 4FeS_2 + 14HCO_3^- + CO_3^{2-} + 10H_2O, \qquad (2)$$
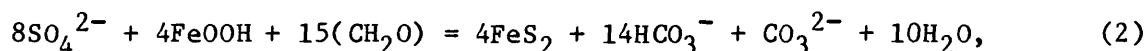
which defines the necessary stoichiometry, but is not a reaction mechanism. For the reaction as written, assuming goethite as the source of ferric iron and glucose as the organic reductant (free energy of formation of glucose from Parks and Huffman, 1932; other free energy and activity data from WATEQF), a free energy of reaction of -370 kcal can be calculated, indicating virtually complete reduction of sulfate in the lignite aquifer at equilibrium. Iron from amorphous ferric hydroxide rather than from goethite would result in a more negative calculated free energy of reaction, and thus an even larger energy source for bacterial reduction.

In the area north of the mine, dissolved sulfate decreases by 3.55 mmol/L between the water table and the lignite. Reduction of this amount of sulfate by the reaction cited above will generate 6.21 mmol/L of bicarbonate and 0.44 mmol/L of carbonate; the carbonate generated is far short of the 3.57 mmol/L needed to complete the precipitation of alkaline earths as carbonates.

The sulfate reduction process could produce different proportions of carbonate and bicarbonate by a sequence of reactions such as the following:
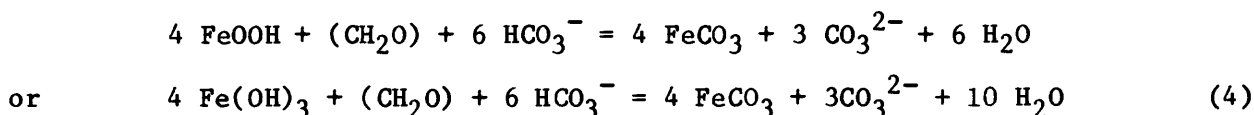
$$2 SO_4^{2-} + 4(CH_2O) = 2 H_2S + 4 HCO_3^- \quad ,$$

then $2 FeOOH + 2 H_2S + 2 HCO_3^- = FeS_2 + FeCO_3 + CO_3^{2-} + 4 H_2O.$

Overall,

$$2 SO_4^{2-} + 4(CH_2O) + 2 FeOOH = FeS_2 + FeCO_3 + 2HCO_3^- + CO_3^{2-} + 4 H_2O. \qquad (3)$$
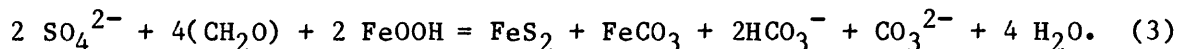
Thermodynamic data indicate that each of the reactions in the sequence should proceed far to the right in the lignite aquifer. The odor of H_2S over most samples from the lignite aquifer demonstrate that this species persists in solution, and that iron disulfide deposition is not necessarily simultaneous with the sulfate reduction process. The hydrogen sulfide can migrate and precipitate iron minerals, and can increase carbonate levels above the lignite seam.

Reduction of 3.55 mmol/L sulfate and deposition of sulfur as iron disulfide by the suggested sequential reactions would provide about half the carbonate required for precipitation of the alkaline earth carbonates in the lignite aquifer. The reactions would also generate 3.55 mmol/L of bicarbonate, although the analytical data indicate a slight decrease in bicarbonate alkalinity between the shallowest wells and the lignite water. A process which could alter the bicarbonate-carbonate distribution is a direct ferric iron - lignite reaction. The reactions noted below would increase dissolved carbonate and also remove an equivalent amount of bicarbonate from solution.

$$4 \ FeOOH + (CH_2O) + 6 \ HCO_3^- = 4 \ FeCO_3 + 3 \ CO_3^{2-} + 6 \ H_2O$$

$$\text{or} \quad 4 \ Fe(OH)_3 + (CH_2O) + 6 \ HCO_3^- = 4 \ FeCO_3 + 3CO_3^{2-} + 10 \ H_2O \quad (4)$$

The free energy of reaction with goethite as the iron source is -16.2 kcal per mol of (CH_2O) consumed; a much larger (negative) free energy of reaction, -48.2 kcal, for the amorphous ferric hydroxide reactant would favor microbial catalysis using the trihydroxide. Activity data for the dissolved species indicate that reaction should proceed far to the right in the lignite aquifer. Removal of 3.85 mmol/L of bicarbonate by reaction (4) would generate 1.92 mmol/L of dissolved carbonate. The combination of reactions (1), (3), and (4) could then produce a lignite horizon water of the observed major constituent composition from recharge at the water table surface.

There exists another class of reactions that could produce the observed concurrent decreases in alkaline earths and sulfate while maintaining the alkalinity at a near constant value. These reactions involve the utilization of carbon with formal valence of less than zero as a substrate during sulfate reduction. The simplest, and most likely, example is methane.

$$15CH_4 + 8FeOOH + 16SO_4^{2-} + 2HCO_3^- = 8FeS_2 + 17CO_3^{2-} + 35H_2O$$

Reduction of 3.55 mmol/L of sulfate by this reaction would consume .44 meq/L of bicarbonate and produce 3.77 mmol/L of carbonate. Precipitation of 3.57 mmol/L of this carbonate with alkaline earth cations would account for the observed decrease in calcium plus magnesium. The resulting aqueous phase would then be depleted by 0.04 meq/L in titration alkalinity (minus .44 meq/L from bicarbonate removal plus 0.40 meq/L from the net 0.20 mmol/L carbonate increase), in good agreement with the observed .06 meq/L decrease (table 12A). Also, increased carbonate in the lignite water would tend to increase supersaturation of the alkaline earth carbonates, a result which is consistent with the WATEQF data of table 15.

There are, thus, two classes of reactions that appear capable of producing the observed within-aquifer changes in water chemistry. The first requires formation of siderite as an integral part of the reaction scheme and is supported by the presence of siderite in many samples based on X-ray diffraction analysis. The second involves microbial utilization of methane during sulfate reduction, which is consistent with the presence of small amounts of methane in all wells sampled.

It is quite possible that both reactions occur in the Gascoyne ground waters, possibly to varying degrees at different locations. It is not possible with existing data to determine the relative contributions of these reactions to the aquifer chemistry.

Reactions in the lignite aquifer also produce changes in concentration of the less abundant dissolved constituents. Halide concentrations in the lignite wells are higher than those in the overlying ground water. Leaching of chloride and fluoride from the lignite probably account for the observed differences. Dissolved potassium, on the other hand, is higher in the shallow water; removal of potassium may be accomplished by ion exchange reactions in the overburden sediments. Silica in the upper water table wells is probably removed by gradual precipitation of chalcedony throughout the aquifer.

The analytical data for the lignite and confined basal-sand waters indicate substantial differences in water compositions of the two aquifer units. North of the mine, water from the lignite aquifer is the only source of recharge to the confined sand, and therefore the observed water-quality differences imply continued mineral-water interaction at and below the base of the Harmon bed. The "net" alkali (alkali less halide) concentration in the basal sand is 3.24 mmol/L greater than the corresponding quantity in the lignite. This increase in alkali nearly balances the observed 1.65 mmol/L (3.30 m equivalent/L) decrease in alkaline-earth solutes, and the close correspondence suggests below-lignite removal of alkaline earths almost entirely by ion-exchange reactions. Other major compositional changes include a decrease of 2.19 mmol/L of sulfate and generation of 4.87 m equivalent/L of alkalinity beneath the lignite seam. Reduction of 2.19 mmol of sulfate according to reaction (2) above would produce 3.83 mmol of bicarbonate and 0.29 mmol (.58 m equivalent) of carbonate. The resulting total alkalinity (lignite water alkalinity plus an increase of 4.41 m equivalents) is in fair agreement with the observed alkalinity of the confined sand waters.

Leaching from the confining underclay probably accounts for observed increases in dissolved halides beneath the lignite. Iron concentrations also are higher in the basal-sandstone waters, although siderite is supersaturated in the confined sandstone aquifer. Complexing of ferrous iron with nitrogen- or oxygen-containing organic products of lignite degradation may stabilize dissolved iron in the highly colored confined sandstone water.

Reactions in the Unconfined Basal Tongue River Aquifer

Irregular distributions of source minerals and mixing with lignite waters and high pH waters lead to a wide range of water compositions in the unconfined basal sandstone in the southern part of the study area. Comparisons of the chemical data averages for the upper 4 m wells with averages for the unconfined basal sand wells provide some evidence of chemical processes occurring in the aquifer. Near-neutral pH in the upper water table wells, in contrast to an average 8.3 pH for the deeper unconfined sand waters, suggests that the oxygen removal process noted above for the lignite aquifer also may limit oxygen penetration into the unconfined basal sandstone. Differences also are observed

between alkali-alkaline earth distributions of the upper 4 m wells and the deeper unconfined sand waters. An average increase in alkali cations of 13 mmol/L and a corresponding decrease of 16 m equivalents/L of calcium plus magnesium in the deeper waters indicate extensive ion-exchange removal of the alkaline earths in the aquifer materials.

Highest sulfate concentrations in the unconfined sand aquifer are found in waters near and downgradient from the unsaturated lignite and leonardite in section 33 (T. 131). The sulfate source for these waters probably is gypsum. Sulfate reduction probably does occur in the unconfined sand, as suggested by the graph in figure 15. However, because of the extreme scatter in sulfate concentrations for individual wells, hypotheses about the nature of the reductants and estimates of the extent of the sulfate reduction are not warranted.

The high pH waters are found near the present natural outcrop of the Harmon lignite. Scoria zones, formed when sections of the lignite were destroyed by natural underground burning, are also present in this area. Houghton (1982b) has observed silica-cemented horizons associated with scoria zones, and extensive hydration and the presence of zeolites in scoria slag in the Gascoyne area. He has suggested that the hydrated scoria slag is a source of siliceous fluids for silica cementation. These fluids, resulting from interaction of recharge water with alkali or alkaline earth silicate, would be strongly alkaline as well as high in silica, and could be the source of the high pH waters in the basal sand.

SUMMARY AND CONCLUSIONS

Recharge to the hydrologic system at Gascoyne originates within a distance of 6 km from the lignite mine. Small streams, rising in hills to the north and east, transport much of the spring snowmelt and the occasional heavy summer rains southward through the mine to eventual discharge into Buffalo Creek in the North Fork Grand River drainage system. Flow of the small streams often declines to zero during the warmer months in this semiarid environment.

Ground water recharge is slight. The local soils are not highly permeable, and evapotranspiration consumes most of the soil water acquired during the growing season. Downward penetration of subsoil recharge is slow in the fine-grained Fort Union formation, and free circulation in the unsaturated zone and in the shallow aquifers is inhibited by numerous thin, impermeable clay and silt strata interbedded with the sands. Perched ground water, common in the area, undergoes considerable evaporation, thereby limiting the volume of subsurface water available for recharge of the water-table aquifers.

With two striking exceptions, ground water wells in the study area contain very little post-1953 water. The exceptional wells are screened in the lignite a short distance north of the mine. Recent dewatering of mine pits may have greatly accelerated flow through particularly permeable channels to produce the approximately 50 percent modern component now found in these well waters.

Water level measurements indicate generally southward flow of ground water, from the recharge area in the hills through the mine to discharge by seepage into the Buffalo Creek tributaries to the south. North of the mine, the basal Tongue River aquifer is recharged by downward leakage through the lignite and confining underclay. Ground-water movement in the southwestern part of the mine area is dominated by a ground-water mound in the unconfined basal sand.

Mineralization of Gascoyne ground water occurs at very shallow depths; the highest total ion concentrations (in reaction equivalents) are found in the shallowest waters. Near-surface source of the dissolved minerals include abundant dolomite, calcite, and gypsum, and occasional surficial deposits of sodium-magnesium sulfate evaporites. Dissolution of several hundreds of mg/L of alkaline earth carbonates is facilitated by unsaturated-zone carbon dioxide pressures greater than .02 atmospheres at some locations in the study area. Ion-exchange displacement of dissolved calcium by sodium permits continued dissolution of gypsum and very high sulfate concentrations in several of the perched waters. Evaporative concentration also contributes to extremely high dissolved solids concentrations in the unsaturated zone.

Waters from the upper water table are usually supersaturated with calcite and dolomite, and slightly undersaturated with gypsum, at a pH near 7 and with a P_{CO_2} greater than 0.02 atmospheres. Deeper in the water table, pH increases, whereas P_{CO_2} and concentrations of alkaline earth ions and sulfate decrease; supersaturation with calcite and dolomite persist at increasing depth below water table. Processes which can account for observed differences between water compositions in the upper water table, the lignite, and the confined basal sand are: 1) Reduction of oxygen near the water table surface, possibly by reaction with siderite; 2) outgassing of carbon dioxide, produced by oxygen removal processes, into the unsaturated zone; 3) ion exchange removal of dissolved alkaline earths and replacement with sodium above, in, and below the lignite; 4) sulfate reduction in and below the Harmon lignite, with precipitation of the sulfur as iron disulfides; 5) an alkalizing reaction in the lignite aquifer, possibly the reduction of ferric iron by lignite to generate siderite and carbonate, or possibly a sulfate reduction reaction utilizing methane, which produces carbonate; 6) leaching of halides from the lignite and the underlying confining clay; 7) precipitation of dissolved silica as chalcedony; 8) ion-exchange removal of potassium in the lignite aquifer; and 9) complexing of iron with organic material derived from the lignite. Oxygen-consuming reactions, ion exchange removal of alkaline earths, and sulfate reduction processes also occur in the unconfined basal sand aquifer. Reactions of recharge water with scoria slag (Houghton, 1982b) may produce the high pH, high silica waters found in the basal sand near the lignite outcrop.

Dissolved oxygen is nearly absent a few meters below water table in the undisturbed ground water system; in this reducing environment, pyrite and ferrous iron are stable, and degradation of the lignite appears to be limited to reactions with ferric iron and with sulfate in infiltrating recharge. Mining exposes initially saturated overburden sediments and lignite to an oxygenated atmosphere. Above the water table in mine spoils, ferrous iron oxidizes rapidly,

disulfides are quickly converted to sulfates, and accelerated interaction of lignite with atmospheric oxygen generates high concentrations of unsaturated-zone carbon dioxide. Dissolution of the abundant calcite and dolomite buffers the pH, and gypsum precipitation and ion exchange reactions on clays and on lignite remove alkaline earth metals from solution in recharge flowing through the spoils toward the ground water discharge area south of the mine. The resulting near-neutral, high sodium sulfate discharge water is chemically similar to that in natural ground water drainage from the unsaturated lignite zone in the southwestern part of the study area. Continued mining will increase the total load of sodium sulfate ultimately delivered to the surface-water drainage system.

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